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An evaluation of solvents in order to increase cavitational effects for the surface treatment of a range of electronic materials

Mkhlef, Bilal

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An evaluation of solvent conditions to increase cavitational effects of power ultrasound for the surface treatment of a range of materials used in the PCBs/electronic industry

Bilal Jaffar Mkhlef

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BILAL JAFFAR MKHLEF

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ABSTRACT

Polymers and ceramic materials are used as substrates in the fabrication of electroless copper plated components for electronic devices. These substrates must be pretreated prior to electroplating to facilitate good adhesion between the substrate and the metal coating. There are a variety of established pre-treatment methods. Most of the industrial methods utilize hazardous chemistry (toxic acids), require long process times, use large amounts of waste water to remove chemicals, and require high temperatures. The aim of this project was to investigate the ability of power ultrasound to pre-treat these materials by utilizing non-hazardous chemistry, lower temperatures and short process times.

In this project four different substrates were investigated; Epoxy resin, ABS, Noryl and Ceramic. The materials were treated with ultrasound under four different conditions (40 °C, 0 °C, freezing before pre-treatment, and the addition of solvent to the bath). The changes on the surfaces were monitored with several analysis techniques including: Weight loss, Contact angle measurement, Roughness measurement, Gloss meter determination, SEM surface analysis and adhesion testing.

The optimum power setting for the epoxy material was found to be between 50 W and 80 W. In addition the most effective surface modification conditions for the Epoxy material was found to be achieved by lowering the temperature to 0 °C during the sonication processes and utilizing a power setting of 50 W. The most effective parameter to employ to surface-modify ABS material was found to be utilizing 5 % gamma-caprolactone solution with a power setting of 50 W at 0 °C. The most effective parameters to employ to surface modify Noryl material was found to be by utilizing 5 % ethylene glycol solution with a power setting of 50 W at 0 °C. Of the four tested materials, the ceramic material was least effected by sonication. The best results for this material were obtained with the frozen samples which were then treated with 50 W power at 0 °C. Solvents results did not shown significant results as those obtained with frozen samples.

The project determined that each material required very specific pre-treatment parameters and demonstrated that surface modification could be achieved at lower temperatures, with far fewer chemicals, and a possibly safer, more economical process than the conventional industrial techniques.

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CHAPTER 1 INTRODUCTION

1.1 AIMS AND OBJECTIVES

The overall aim of this project was to develop an optimised sonochemical surface modification process which operates at low temperature, uses non-hazardous chemistry and short treatment times. This was done by investigating the optimisation of sonochemical parameters such as ultrasonic intensity, temperature and the effect of adding solvents to DI water for sonochemical surface modification processes.

The objectives of this project were to:

1- Sonochemically surface modify a range of materials used in electronic, metal finishing and automotives industries.
2- Optimise the ultrasonic intensity for each material.
3- Lower the process temperature and to employ less hazardous chemistry.
4- Evaluate the effect of prior freezing of the samples on the surface modification process.
5- Determine the effect of added solvents to the DI water on the surface modification process.

A range of samples were chosen in this study. Primarily for their uses in the electronics industry and also to offer a breadth of sample type with respect to their individual properties in order to try and identify the effect of sonication conditions on them.

For example:-

Epoxy (high Tg resin) is used in the multi-layer boards (MLBs) and printed circuit boards (PCB_S) industries and these are involved in all electronics instruments such as mobile phones, laptops and TVs.

ABS (Acrylonitrile Butadiene Styrene) is widely used in the metal finishing and automotive manufacturing industries and is utilized in personal computer (PC) cases, mobile phone casings and their interior components

Noryl (Polyphenylene ether – polystyrene) is being utilized in the moulded interconnected devices or as printed circuited boards within the electronic manufacturing industries.

Ceramic material (Zirconium Tin Titanate) is utilized in the waveguides, aerials and antennas production industries

1.2 ELECTRONIC MATERIALS

Most electronic devices e.g. computers, laptops, radios, calculators, mobile phones etc, utilize a number of plastics and polymers in their fabrication. Generally, most of these plastic/polymers are non-conductive materials. These materials are often the base material/substrate onto which is placed an electronic circuit and for this reason they must be metallised. The electroless plating processes is the most widely used method to produce conductive layers on the surface of these materials and to enable interconnection between different electronic components placed on top of these polymers. Before describing what electroless plating is, it would be an important thing to take a close view of the materials which have been involved in this project and the electronics or other applications they involved in. Acrylonitrile-Butadiene-Styrene (ABS) plastic has been widely used in the metal finishing and automotive manufacturing industries (Groshart 1972) and is present in personal computer (PC) cases, mobile phone casings and their interior components. Epoxy (high Tg) resin is used to manufacture multi-layer boards (MLBs) and printed circuit boards (PCB_S) and these are involved in all electronics instruments such as mobile phones, laptops, TVs, etc. These are used to electrically connect electronic components by utilizing conductive traces which have already been patterned onto glass-epoxy resins (non-conductive) (Goosey and Poole 2004). These conductive traces are made up of copper or very rarely nickel which been produced via an electroless plating process. Noryl HM4025 (Polyphenylene ester / polystyrene) has been utilized in the moulded interconnected devices or as printed circuited boards (Cobley and Mason 2007). Dielectric ceramics such as Zirconium Tin Titanate have been utilized in the manufacture of waveguides, aerials and antennas. Most of the mentioned materials are electroless plated either with copper or nickel.

Picture 1, Printed circuit board (Clarydon Electronic Services n.d.)

Generally, it is difficult to obtain sufficient adhesion between these materials and the subsequent electroless copper plating without pretreatment of these substrates and the bond strength between the metal plated and substrate has a large significance in the final product whether this is utilized in a decorative technique or as a p rinted circuit board (Teixeira and Santini 2005). Consequentially, the surfaces of these materials are often surface modified by attacking the surface of the material with strong oxidizing agents in order to produce an etched surface to ensure the subsequent electroless plating adheres strongly onto the surface of material. The strength of mechanical bonds occurring when the metal is plated on the etched surface plays an important factor in securing good adhesion between the material surface and the electroless plating. In addition, chemical bonding may also enhance the adhesion (Siau *et al.* 2004a). Neutralisation is a prime essential step which needs to be applied after the material is treated in order to remove all strong oxidant agents or acids and others chemical associated with treatment process in addition to the residues formed via treatment.

1.3 ELECTROLESS PLATING

Briefly, the electroless plating processes could be defined as a processes which does not involve using an external electrical power in order to deposit a metal (generally copper or nickel) on the surface of materials to produce conductive layer. In these processes, the material (polymer) which has been surface modified is soaked in conditioner solution (surfactant based bath) which improves the catalyst adsorption. Rinsing steps are then applied to the material, to wash off excess chemicals, and then it is immersed in the predip solution to protect the following catalyst solution from contamination. The catalyst (Sn/Pd) colloid solution is then applied in order to deposit Pd on the surface of material and rinsing steps are carried out. Eventually, the electroless copper solution is employed so as to form a copper (conductive) layer at the surface of material and then a final rinse with water is applied to clean the material surface.

1.4 SURFACE MODIFICATION IN ELECTRONIC AND PCBs MANUFACTURING

Since approximately 1960, the metallization of non-conductive materials by electroless plating has attracted much attention due to the fact that it is used in a wide range of technology applications such as the fabrication of printed circuits in the electronics and microelectronic manufacturing industries. It has allowed the properties of a polymeric material (e.g. lightweight,

low cost and non-conductive) to be combined with those of metal (e.g. conductive, wear resistant. The increasing demand for high interconnection densities and further growth in polymer synthesis, which could produce more new materials suitable for high technology industries, means that there is more pressure on both industry and researchers to investigate the most convenient method to metallize these materials.

A cost effective and widely used method of metalizing Polymeric materials is known as electroless plating. Good adhesion between the metal (e.g. copper) and the polymer is of prime importance for the reliability of the interconnection (in PCB manufacture) and subsequently electroplated copper (Siau *et al.* 2004b). Therefore, it is necessary to form a mixture of physical and chemical bonds between the polymer and the plated metal. Hence, the polymeric substrate is frequently roughened or textured to produce a mechanical bond, whilst changing the chemistry of the surface will form a c hemical bond between the substrate and its coating in order to improve the adhesion (Siau *et al.* 2004b).

There are many different techniques which have been employed for the purpose of surface modification for different kinds of polymers. For instance, polymers have been surface modified by using different methods such as chromic acid, sulphuric acid and alkaline permanganate (Mandich and Krulik 1992). Some of these have been utilized successfully during the last few decades in electronic manufacturing and are still employed nowadays. However, increasing environmental and health and safety legislation such as the requirements to prevent any emission or toxic substance into the general environmental or the restriction of hazardous substances (RoHS) directive has been one of the most important reasons why researchers and industries have investigated new methods or processes (Cobley 2007a).

It is known that most of the earliest electronics devices such as computers had a large room size machine. These contained miles of wiring so the maintenance of those devices involved replacing most of these wires, which was a problematic step for these industries particularly from the economic point of view. With the revolution in hardware design the big size of these machines has been reduced and the big mass of wiring has been replaced by the production of double and multi layer circuit boards. With further invention of the double and multi layer of

these circuit board and with the fact that the majority of manufacturers of PCBs are now involved in using multi layers boards, intensive work has been applied in order to investigate the most convenient method to build up an interconnection amongst these layers. Traditionally this has been done by drilling.

Picture 2, Holes inside PCB between different layers (Holden 2009)

So the main purpose of these holes was to build up an interface between the top of material layer and the bottom layer in the double circuit boards and also provide an interconnection between layers when a multilayer circuit boards is utilized (Jawitz 1997). During the drilling operation, heating occurs which could melt some of the resin of the material (Lee *et al.* 2002) particularly if the heating temperature has moved above the glass transition temperature (Tg). These resins smeared around the hole walls which then means that subsequently drilled holes have smearing across their inner layers. As a result when the material (which contains the holes) is later electroless copper plated this smear prevents an electrical connection between the inner layers and the hole wall of the drilled holes. Therefore, this resin must be removed so the interconnection could be made between the inner layers and the electroless coating. Although the heating occurring during drilling can be prevented via cooling the bits, clean layers and an assured connection between the layers is a prime requirement for the electronics manufacturers. This means that the removal of this resin must be achieved and for this purpose the desmear processes is employed (Jawitz 1997). In the next few pages, short descriptions about these methods are described.

1.5 TRADITIONAL SURFACE MODIFICATION

There are various traditional methods for promoting adhesion between the coating and its substrate. The choice of method depends on the type of material which is utilized for a specific

purpose. Each polymer and ceramic has its own surface modification treatment specifically adapted to its characteristics. In the traditional processes most of the treatment methods are performed by utilizing solutions which contained different surface modification chemicals. The substrate must be immersed in these solutions in order to change the property of surface (chemically or physically) and these substrates are later electroless copper plated. For this reason, these processes were known as a wet chemical processes.

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1.5.1 Wet Chemical processes

These processes are the most traditional methods which have been utilized in the surface modification processes for the last few decades (Cobley 2007a). The principle of this technique involves exposing the polymers to an etching solution such as a strong oxidant like sulphuric acid or chromic acid (Karas 1992), and then the substrate is further cleaned by chemicals to remove any residues.

The subsequent bond formed between the metal and the polymer surface results from the roughness created on the surface which provides anchoring i.e. a physical or mechanical bond. The change in the surface chemistry allows for chemical bonding between the substrate and the electroless copper (Siau *et al.* 2004b). Each individual polymer may require different processes for surface modification. Many wet chemical processes have been successfully and widely used via the industries but, also there are few alternative processes which have been applied in order to surface modify polymers.

1.5.1.1 Surface modification using chromic acid

Use of Chromic acid (CrO_3) could be considered as one of the oldest and the most commonly employed methods to surface modify certain polymers such as ABS (Ghorashi 1977) although it has also been used in the desmear processes for (PCB_S) manufacture. To understand the mechanism which occurs over the ABS surface via utilizing chromic acid, it is necessary to consider the structure of this polymer. ABS was first introduced in 1948 by U.S. Rubber under the brand name of Royalite. Although it was not the first plastic to have been produced for the purpose of plateable plastics, it has been deemed as the first plastic which offered good strength, excellent hardness and outstanding adhesion if a good pre-treatment for the surface was applied

in advance. The ABS plastic is a polymer which consists of three monomers acrylonitrile, butadiene and styrene. These monomers can not be polymerized simultaneously; instead, each monomer creates a co polymer with the other monomers. T he acrylonitrile contributes to the chemical resistance and the hardness of the plastics, the butadiene participates in the toughness and to the resistance of the plastic's and the styrene participates in hardness of the plastics.

Figure (1) ABS chemical structure (Abenojar *et al.* 2009)

ABS generally is a r obust plastic with good chemical resistance to both mineral acids and alkaline (Groshart 1972). Brief knowledge about the structure of ABS was very important to understand the mechanism of the way which chromic acid reacts with the ABS surface. Chromic acid is a strong oxidizing agent and by dipping ABS material into a ch romic acid bath, the copolymers which are composed with butadiene are dissolved due to chromic acid attack (via oxidation). These copolymers dissolve faster than other copolymers which do not have butadiene within their structure and generate a surface topography consisting of microscopic cavities or pores on the ABS surface. On the other hand, chromic acid breaks down the double bonds C = C

in butadiene so producing these microscopic cavities. These microscopic cavities produce a rough ABS surface into which subsequent coating can anchor (see pictures 3 and4). It is believed by many researchers (Elmore and Davis 1969, Bucknall, Drinkwater and Keast 1972) that this anchoring (physical bond) is the most important reason for the subsequent electroless copper adhesion into the ABS surface. The following equation (below) shows the oxidising reactions which occurred when ABS is immersed in the bath contained the mixture of chromic acid, sulphuric acid and water (the etchant solution); (The $C_{15}H_{17}N$ is the formula of ABS).

$$\mathbf{2\ C_{15}H_{17}N + 81\ H_2SO_4 + 54\ CrO_3 \longrightarrow 30\ CO_2 + 2\ NO_2 + 98\ H_2O + 27Cr_2(SO_4)_3}$$

In spite of the fact that this mechanical bond seems to be the more effective factor in achieving good adhesion to the ABS substrate, there are researchers who consider that beside the mechanical bonds produced by chromic acid, an additional chemical bond is produced by altering the ABS surface from hydrophobic nature to hydrophilic nature (Mandich and Krulik 1993, Soubestre and Khera, 1971) and this is believed to be due to the generation of polar groups on the ABS surface by adding the etchant solution (chromic acid, sulphuric acid and water) (Mandich and Krulik 1993). These polar groups include; carboxyl group ($R\text{-}CO_2H$), aldehyde group (R-COH) and sulphate group ($R\text{-}SO_3H$) which enhances the ability of a good adhesion between the ABS and the electroless copper to be formed (McCaskie and Tsiamis 1982).

Picture (3) ABS before treatment

Picture (4) ABS after 15 minutes treatment with chromic acid

Picture (3) and (4) (Cobley2007b)

Using the chromic-sulphuric acid process could be considered as the cheapest and most convenient process in order to surface modify ABS particularly as it leads to the production of a good rough surface and eventually to good adhesion between ABS and its coating. Unfortunately the use of this process is now becoming problematic particularly with the fact that employing chromic acid generates hexavalent chromium residues (Cr^{6+}) which are very toxic and can produce serious operational problems such as poisoning the subsequent electroless plating process (Cobley 2007a). Although the neutralisation step (utilizing reducing agents solution such as sodium bisulphite) is always employed to remove hexavalent chromium residues (Weiner 1977), this step produces an additional waste problem which produces further environmental problems. A large amount of water is also required during this process for rinsing which introduces an extra expense which is undesirable from a commercial point of view and the water becomes contaminated with chromic acid residues (Cobley 2007a).

Clearly there are environmental and heath and safety issues associated with this process which is also operated at high temperature (60-90 C^o) and therefore requires energy for heating. It would be desirable therefore to replace this process by new methods.

1.5.1.2 Surface modification using sulphuric acid

Desmearing using sulphuric acid was one of the wet chemical process successfully employed in the PCB (Angstenberger 1994) and MLB industries for epoxy materials. The sulphuric acid desmear system typically involves utilizing three steps in addition to the rinse step. The first step involves using sulphuric acid at concentration approximately 90-92% or higher and the rinse step is then expected to be highly acidic due to the amount of sulphuric acid which have been removed. The second step involves utilizing a tank containing an alkaline solvent cleaner. This is an essential to remove the reprecipitated epoxy that drops out of solution when the sulphuric acid is diluted less than 92% during rinsing (McCaskie 1989). The boards are then rinsed but this rinse then becomes contaminated with solvent (from the alkaline cleaner) and the precipitated epoxy (Mandich and Krulik 1992). The last step is to utilize the glass etch solution which consists of ammonium bifluoride and hydrochloric acid.

The surface properties of epoxy resin, like most polymers, have an important impact which determines the adhesion between the material and the subsequent coating. On other hand good care must be taken while drilling the hole through the epoxy resin wall and good pre-treatment processes must be applied in order to achieve good adhesion (Haug *et al.* 1989). There are a few advantages of utilizing sulphuric acid for example, (i) this acid is proportionately not expensive, (ii) fast epoxy removal and finally (iii) it is operated at room temperature.

Despite these advantages, there are several disadvantages produced if this process is utilized such as; (i) if the concentration of sulphuric acid is below 90-92% the solution loses effectiveness (Jawitz 1997), (ii) process control problems as sulphuric acid absorbs water from air which decreases the solution activity and leads to a change in etch rates (therefore a small amount of sulphuric acid is always added to the solution in order to keep it as effective as possible, and (iii) most importantly it produces a glass-smooth hole wall which decrease the adhesion strength between the epoxy resin and the subsequent electroless copper plating (Deckert 1987).

1.5.1.3 Surface modification using alkaline permanganate

For several years, particularly with the appearance of the multi layer boards, the use of swell and etch desmear processes have been accepted in the electronics and PCBs manufacturing due to the quality and the cost improvements compared with previously mentioned methods. This wet chemical method is used across PCBs industries and has been utilized in order to surface modify several types of polymers such as low Tg laminate made using bisphenole based epoxy resin which have a glass transition temperature of 150^{o}C (Goosey and Poole 2004) and polyimide polymers. The concept of this system is using the permanganate alkaline as a strong oxidant and solvent to attack the polymers surface and remove resin smear produced by the drilling processes (see 1.3.1.2).

Alkaline permanganate system consists of three stages The first stage utilizes a solvent which swells the epoxy resin to prepared it for the permanganate etch step. Solvent solutions used are based on butylcarbitol, glycol, N-methyl-2-pyrolidone (NMP) or glycolesters, methyl ethyl ketone (MEK) -alcohol mixture, dimethylformamide (DMF), MEK-surfactant mixture, alcohol and DMF or glycol mixture and sodium hydroxide (NaOH) -NMP glycolester (Mandich 1994).

This step is essential to produce a rough epoxy surface. The swelling step efficiency is not dependent just on the type of material (polymer) which has been utilized. Actually, it has been found that the choice of solvent for swelling polymers is considered as an additionally effective factor which determines the quality of this method. For low Tg it has been reported that the glycol ether has been widely employed in the swelling step as glycol ether has the same solubility parameters to the low Tg epoxy resin (Goosey and Poole 2004).

To understand the mechanism beyond this swelling step, it has been suggested by Thorn (Thorn 1991) that the weaker secondary bonds in the polymeric network (polymer - polymer bonds) are replaced by the polymer-solvent bond which produces a swelled polymer surface when solvent is added. On other hand, the capability of the solvent to change the secondary bonds could be defined as the solubility parameters for the solvent which is dependent on the relative similarity in durability of these bonds. In addition to the swelling effect caused by this step, this step participates in lowering the surface activity of the surface which enables the next etchant step to attack the swelled surface. The swelling step is found to be more effective if the time of the material immersion in the solvent is increased. The typical time for this stage seems to be approximately 5-15 minutes but if more time is applied, the subsequent electroless copper layer would be less achievable as the surface of the material would be saturated with solvent and the following etchant step would be less effective (Thorn 1991). The system is operated at high temperature 75-85 ^{o}C (Goosey and Poole 2004).

The second step of this method involves using the etchant step. This is operated by utilizing the alkaline permanganate (normally either potassium or sodium) as an etchant solution. Increasing the concentration of the etching solution normally increases the etch rate. Although this seems to be an accepted way for increasing the etchant rate, but concentrated sodium permanganate is very harmful. Considering that sodium permanganate is more expensive than potassium permanganate, it is more usual to utilize potassium permanganate in the PCBs industries.

Alkaline potassium permanganate is a powerful oxidizing agent and when the polymer is immersed in this solution it will attack or etch the swollen resin produced by the solvent (weaker

secondary bonds (polymer-solvent bonds). Consequently, the resin smears on the surface and on the hole wall are removed and a rough texture results which is better for adhesion.
This surface morphology is believed to be an important factor for improved adhesion with the subsequent electroless copper. Goosey and Poole (2004) have referred to this surface morphology as a 'honeycombed' (Picture 5).

Picture 5 Honeycombed surface morphology at Epoxy resin surface (Goosey and Poole 2004)

The rate of the epoxy resin removal is controlled via the immersion time and temperature in addition to controlling the solution concentration (Wynschenk and Delgobbo 1986). The alkaline permanganate step is operated at high temperature 75-85 ^{o}C and with immersion times of approximately 5-15 minutes (Goosey and Poole 2004). During this etchant step or oxidising process, the permanganate ion is reduced to manganate which later reacts with water to produce insoluble manganese dioxide as shown in following reaction;

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

Manganese dioxide is produced as a black sludge and causes a r eduction in the etchant concentration and can also be a source of poor adhesion after subsequent plating.

Eventually, in order to remove manganese dioxide residues from the surface of the material and from the through holes and to ensure that the surface is clear, the final neutralise step is carrying out. This could be achieved by adding a mixture of sulphuric acid and hydrogen peroxide

(Goosey and Poole 2004) which alters the insoluble manganese dioxide residues to soluble format and these could be removed by simply rinsing with water. The process is operated at 25 ^{o}C and has an immersion time of approximately 2-5 minutes. The following reaction describes the mechanism of this formation;

$$MnO_2 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O_2$$

Swell and etch desmearing has a slow operation time, typically 25-30 minutes (in total) compared to 15 minutes with sulphuric and chromic acid, and uses a very strong oxidizing agent (alkaline permanganate). It is also more expensive to operate than the previous methods (Mandich and Krulik 1992). However, despite these negative effects, the alkaline permanganate etch is believed to be the best wet chemical process compared to the two previous processes (chromic acid and sulphuric acid surface modification) due to a few reasons such as, (i) this method is very controllable and produces excellent texturing and reliable smear removal, (ii) it works with many types of polymers such as epoxy and Noryl while the previous methods work only with specific materials eg. (chromic acid with ABS) and (sulphuric acid with epoxy), (iii) the solvents utilized could be recycled or incinerated (Mandich and Krulik 1992), (iv) the entire chemical hazardous for the waste produced is less than previous methods taking into consideration the hazardous nature of chromic acid and the huge amount of epoxy toxic residues produced at the final stage of sulphuric acid system. The soluble manganese residues are relatively easy to waste treat which mean that it is safer to use this system rather than others from the disposal and process aspects. The adhesion rate achieved via this process is significantly better than previous methods (Deckert 1987).

The mechanism by which acceptable adhesion is obtained using swell and etch is believed to be due to the physical bonds occurring at the rough surface of the treated material in addition to the possibility of chemical bond generation (see 1.5.1). The following pictures show the surface morphology achieved via applying this system. The pictures after treatment indicate clearly that a rough surface has been achieved (etched surface).

Picture 6 Epoxy resin before treatment

Picture 7 Epoxy resin after 15 minutes treatment with alkaline permanganate

Picture 8 Noryl before treatment

Picture 9 Noryl after 15 minutes treatment with alkaline permanganate

Pictures 6, 7, 8 and 9 (Cobley 2007b)

In recent years, in response to a big demand from technology manufactures in conjunction with the development of smaller and more technical electronic devices, standard Tg laminate epoxy resins have been mostly replaced by newly developed high Tg resins. These high Tg resins have more thermal stability than standard Tg and have glass transition temperature of 200^{o}C and in special cases this could reach 300^{o}C.

As it was mentioned above, the surface modification process using alkaline permanganate is one of the most common and widely used processes in PCB manufacturing. However when this system is applied to treat the new high Tg epoxy resin it is not as effective for desmearing and produces a reduced roughness for the material (Patton and Suen 2004). This is believed to be because the high Tg materials are more chemically inert due to the presence of more crosslinking of polymer fibers.

In addition, the surface morphology produced after the treatment does not appear to give a clear honeycombed structure (see picture 10) compared to that mentioned previously (see picture 5).

This means that adhesion of electroless copper is not as good compared to low Tg and the smear removal is less. However, because they are high Tg materials, they are expected to have much less smear, and because they are more stable they do not move/melt so much during thermal shock. Due to these properties of high Tg resin, a lower level of adhesion can be viewed as a slight disadvantage compared to other benefits of this material.

Picture 10 Surface morphology for high Tg resin (Epoxy) after treatment (Goosey and Poole 2004)

Employing strong solvents in the swellant step to treat the new resin has shown a slight effect on the weight loss readings, which have been increased, and means that more epoxy resin or smear from the surface and the holes wall has been removed. This was associated with reduced roughness on the material surface which as mentioned previously, is one of the most important reasons for the subsequent electroless copper plate to be adhered on the material surface. Utilizing stronger solvents introduced a waste problem and produces an extra cost. Alternatively, it has been found that increase the immersion time or the permanganate solution concentration also improves the weight loss and produces an acceptable roughness on the surface. In the case of increasing the solution concentration, this introduces a control problem as the concentration is raised by almost double, and the material might be attacked strongly via this factor, so more care of other parameter must be considered and these are not always suitable for the technology industries especially from the economic point. Doubling the immersing time has been found more practical than the increase the concentration as it is easier to be controlled (Patton 2007). The PCBs manufacturers are still looking for more economical convenient methods for producing a good rough surface, to achieve as best as possible an adhesion level and to be a suitable process from an economic point of view (Cobley 2007a)..

1.5.1.4 Surface modification using hydrofluoric acid

The ceramic material is an inert chemical material which has been used in scientific research, and by waveguide/aerials manufacturers. An example of the surface treatment process for this material is as follows. Firstly the ceramic is soaked in a solution containing the following compounds; sodium carbonate (Na_2CO_3) 50 g/ l, sodium hydroxide (NaOH) 30 g/ l, sodium phosphate (Na_3PO_4) 30g/l and sodium silicate ($Na\ SiO_3$) 10 g/ l. This solution is employed to clean the ceramic substrate (remove greases) and it is operated at 85 ^oC and taking approximately 60 minutes. A rinsing step using distilled water is applied after this step. The second step uses the roughness solution mixture and consists of potassium dichromate ($K_2\ Cr_2\ O_7$), sulphuric acid and hydrofluoric acid (HF). It is operated at 80 ^oC for 2-30 minutes, rinsed in distilled water, boiled in water (15 minutes) and is then followed by an ultrasonic cleaning for 45 minutes (Shi *et al.* 1997). Different mixtures have been used instead of sulphuric acid and hydrofluoric acid, e.g. nitric acid (HNO_3) and fluoroboric acid (HBF_4) (Baumgartner 1989). This solution attacked the ceramic surface strongly which caused damage to the surface if the thickness of the ceramic was less than 1.00 mm. Although this etching solution was accompanied by ultrasonic agitation but, ceramic particles which remains on the ceramic etched surface need to be removed as the ceramic etched particles causes a decrease in adhesion with subsequent plating. Consequently, utilizing the potassium dichromate, sulphuric acid and hydrofluoric acid mixture has been more accepted (Shi *et al.* 1997). Controlling the time for exposing the ceramic to this solution must be taken in account in order to improve the roughness on the ceramic. The colour of roughened ceramic after boiling in water could be a good indicator for controlling the process. By the end of the etchant step a sensitization stage is carried out to produce some type of tin ion (Sn^{+2}) that is helpful in the subsequent electroless plating. This is achieved via sensitized a roughened ceramic in a solution of tin (II) chloride ($SnCl_2$) mixed with hydrochloric acid(HCL) and diluted by distilled water (Shi *et al.* 1997).

Picture 11 shows the ceramic surface before treatment. Picture 12 represents a ceramic surface which has been treated with a solution of 15 % hydrofluoric acid diluted by DI water. The treatment has been performed for 15 minutes and also at room temperature.

Picture 11 Ceramic material before treatment

Picture 12 Ceramic material after 15 minutes treatment with sulphuric and hydrofluoric

Pictures 11 and 12 (Cobley 2007b)

It has been reported that the roughness produced on the ceramic is believed to be because the etchant attacked the hollows of the grain boundaries area. The crevices which are produced via the etching step occur on the grain boundaries. The grains themselves are not etched effectively (Honma and Kanemitsu 1987). However it is now believed that the etchant solution attacks the hollows of the grain boundaries area and the grain boundaries themselves and the crevices are distributed on the whole ceramic surface rather than being concentrated on the grain boundaries area only. The adhesion obtained by subsequent plating is due to the mechanical bond occurring when the electroless plating fills the crevices (holes) on the ceramic surface. It has been indicated that increasing the roughness doesn't necessarily result in good adhesion (Shi *et al.* 1997). This could be explained as the more roughness on the ceramic surface indicates that more holes or may be biggest holes could be formed and when the subsequent plating is applied, some of these holes might not be filled resulting in a non acceptable level of adhesion.

1.6 ALTERNATIVE SURFACE MODIFICATION METHODS

It has been mentioned previously that wet chemical processes have been performed widely across the electronics, metal finishing and PCBs industries and there are several reasons for this such as: (i) the low price of these processes compared to others, (ii) an acceptable level of surface modification (morphology) is produced, (iii) good results in terms of adhesion with the electroless plating is achieved via these processes. Nevertheless, there are also several disadvantages associated with these processes such as: (i) long process times, (ii) operation at high temperatures, (iii) utilization of high amounts of water for rinsing steps(Shi *et al.* 1997), (iv)

using hazardous chemistry such as chromic acid, sulphuric acid, hydrofluoric acid etc which impose a s erious waste treatments problems in order to remove these hazardous chemicals compounds from the manufacturing lines.

Taking in account these disadvantages, and considering new strict environmental and health legislation, there is a big demand to replace these hazardous processes by alternatives methods which are more convenient for the manufacturing from the environmental and economic points of view. There are several methods which have been applied in order to surface modify various types of polymeric materials including Electrochemistry, Plasma, Ozone and UV, Photocatalytic treatment, Corona discharge and Sonochemistry.

1.6.1 Electrochemistry method

It has been mentioned in previously that the traditional surface modification treatments rely on the usage of strong oxidizing agents. Hence, it is reported that using silver ions (Ag II) to surface modify polymers is feasible due to the strong oxidizing nature of these ions. This system has been firstly disclosed in 1997 (Brewis, Dahm and Mathieson 1997). Silver ions have been generated by anodic oxidation of silver nitrate in dilute nitric acid. It has been found that when these ions attacked some types of polymers or plastics, oxygen groups are introduced such as carboxylic, hydroxyl and carbonyl groups (Brewis, Dahm and Mathieson 1997). An acceptable level of adhesion has been achieved as these groups enhance the adhesion level between the material surface and subsequent plating as it was mentioned previously. This work has been operated at temperature of 60 ^{o}C (Brewis *et al.* 2000a). Nevertheless, it has been found that these ions are not able to attack (oxidise) polymers consisting of straight chain alkanes such as dodecane (Paire *et al.* 1997). Another work has been carried out to anodically generate nitrate radical (NO°_3) which also has an oxidizing nature and able to oxidize the polymer surface at room temperature (Brewis, Dahm and Mathieson 2000b).

More interesting and in conjunction with above works, it has been reported by Graves *et al.* (2001) that the silver ions generated as mentioned previously could oxidize the ABS surface producing a micro etched surface. This surface has produced an equivalent adhesion level to that produced via chromic acid surface modification (Graves *et al.* 2001). From an environmental

point of view, using this method introduces serious problem from using nitric acid which is very toxic acid in addition to the problem associated with waste treatment (it will contain an amount of this acid) besides the high cost of this method.

1.6.2 Ozone and UV/Ozone method

In 1985, the use of ozone (O_3) for surface modification purpose was discussed (Jobbins and Sopchak 1985). This work has utilized ozone in order to surface modify ABS, Noryl and other types of plastics. The concept of this system is to use ozone an oxidizing agent that is used to etch the surface of material (Jobbins and Sopchak 1985). The mechanism of this method when it reacts with ABS for instance could be described as the following: t he ozone reacts with butadiene copolymers on the ABS surface forming an unstable ozonide (see following reaction).

(Jobbins and Sopchak 1985) removed for copyright reasons

This ozonide formed is decomposed to give an aldehyde structure which then is oxidised to an acid and forming (CH_2─COOH). This compound is then reacted with sodium hydroxide solution which produces the sodium salt of the previous acid (CH_2─COONa) and this salt is a dissolvable solution which can be removed from the surface of ABS and results in presents an etched and hydrophilic surface. This system is unlike the previous wet chemical processes as it avoid utilizing very hazardous chemicals such as chromic acid which is a prime requirement from the environmental and health point of view. It has been demonstrated that the ABS surface produced by this method is evenly attacked and it has a more aesthetically pleasing appearance than the chromic acid treatment. This plays an important factor as it could enhance the adhesion with the subsequent electroless plating (Jobbins and Sopchak 1985).

The ultraviolet ozone process (UVO) has been used initially to surface treat wood fibers (Bradley, Clackson and Sykes 1993). Later on, this process was employed to treat a few types of polymers such as polyethylene polymer. It has been demonstrated that a good adhesion between the polymer surface and the plating is achieved (Mathieson and Bradley 1996). This acceptable level of adhesion is believed to be caused by producing chemical oxygen species on the surface due to the oxidation effect of this treatment. These chemicals species include; ether group and carbonyl group. More interesting, the surface wettability has been increased during this process. This is associated with the surface energy and this plays an important factor in improving the adhesion (Abenojar *et al.* 2009).

From the economic view point, this is an expensive surface treatment method compared to traditional methods such as using chromic acidand would add to industrial production costs. In addition, there is a lack of general information about the procedure and the effect of this system to treat other types of polymers.

1.6.3 Plasma treatment method

Plasma surface treatment which is a dry treatment system could be described as a unique and efficient method in order to surface modify. ABS has been treated via this method and the results obtained have shown some significant effects for example (i) removing a sufficient amount of material from the surface in very short time (2 minutes), (ii) an acceptable surface roughness is achievable,(iii) could produce good adhesion between the ABS surface and subsequent plating (Villamizar, Rojas and Frias 1981). It has been reported that this method has been applied to surface modify various polymer materials such as poly ethylene terephthalate (PET) (Oh, Kim and Kim 2002, Yang *et al.* 2009), polyvinylidene fluoride (PVDF) (Nicolas-Debarnot *et al.* 2006) and ultra-high molecular weight polyethylene UHMWPE (Liu *et al.* 2010)

Basically, this system is changing the treated surface via two types of effect; physically (which produces a good surface morphology (roughness)) and chemically (due to the production of polar groups on the surface). These polar groups such as carboxylic and aldehyde groups are the main reasons to produce a hydrophilic ABS surface which plays an important factor in the improved plated metal adhesion and roughness (Abenojar *et al.* 2009). The wettability (contact angle) of

the surface was demonstrated by employing contact angle instrument and the surface roughness was demonstrated via scanning electron microscope (SEM).

In spite of the good level of surface roughness and the wettability which was also increased, there are two essential factors that need to be taken in account which make this system not a practical one compared to the wet chemical processes. Firstly, a strong adhesion between the polymers and subsequent electroless plating is not guaranteed via this process (Rozovskis, Vinkevicius and Jaciauskiene 1996, Ge, Turunen and Kivilahti 2003). Secondly, considering the economic points of view of the industries involved in electronics materials production, this method is very expensive to set up in comparison to wet chemical process.

1.6.4 Photocatalytic method

Photocatalytic process could be described briefly as an oxidant reaction occurring when the polymer material is immersed in a solution contained titanium dioxide particles (TiO_2) and then ultraviolet (UV) is applied. The photocatalyst solution (titanium dioxide) is prepared initially from the reaction between the ammonium hydroxide (NH_4OH) and titanium oxychloride ($TiOCl_2$). A solution of titanium hydroxide is produced and by monitoring the pH and adding hydrogen peroxide (H_2O_2) solution, a yellow titanium dioxide precursor is produced which is then heated in an autoclave at 120 ^oC for 10 hours (Kim *et al.* 2006). It has been demonstrated that when titanium dioxide and UV (with an appropriate wavelength) is applied, hydroxyl radicals are formed(Kim *et al.* 2006). These species acts as very strong oxidizing agents which attack the surface of polymer materials. Consequently, an oxygen species such as carboxyl and aldehyde groups are generated (Carp, Huisman and Reller 2004).

It has been confirmed that the intensity of UV light is decreased if the titanium dioxide concentration is increased. This is believed to be occurred because of the dispersion of the light by titanium dioxide particles (Bessho, Koiwa and Honma 2006). Epoxy resin material has been treated with this technology (Kim *et al.* 2007) in addition to ABS (Kim *et al.* 2008) and both material presented similar results. It was demonstrated that the wettability in both materials was increased via utilizing contact angle instrument. The oxygen species such as carboxyl and aldehyde groups produced on the surface of material are the main reason for the hydrophilic

surface and these species play an important role in improving the adhesion between the material substrate and subsequent electroless plating. In spite of the low cost, high chemical stability and the ability if utilizing the sunlight as the irradiation source in this process, the adhesion obtained via this technology is typically not as good as the adhesion obtained via wet chemical process (Cobley 2007a). This could be due to the surface morphology (roughness) occurring after treatment which is almost unchanged compared to the surface before treatment meaning that there is not enough physical bonds between the surface and the electroless plating as it has with wet chemical processes.

1.6.5 Corona Treatment

Corona or corona discharge treatment is another treatment technology employed to surface modifies several polymeric materials such as poly propylene (Stroble *et al*. 1989). Styrene-Butadiene-Styrene rubber is also reported to be surface modified by Corona discharge method (Romero-Sanchez, Pastor-Blas and Martin-Martinez 2003). This method consists of the ionization of the air molecules when an electric discharge of high voltage is applied between two close electrodes. When the sample of the tested material is placed between these electrodes, the charged particles crash on the surface of the material and initiating a radical mechanism reaction. The radical reaction is the main reason behind the ability of this method to surface modifies polymeric materials as these radicals react with the surface and generate polar groups such as COH, –COOH, and COC group (Romero-Sanchez, Pastor-Blas and Martin-Martinez 2003). The production of these chemical groups was monitored by using X-ray Photoelectron Spectroscopy (XPS). These groups are known for their ability to introduce a hydrophilic surface (wettability surface) and this can enhance the adhesion between the surface and the plated metal. (Abenojar *et al.* 2009). Generally, the corona discharge treatment is fast and is easy to perform, can be operated at atmospheric pressure and does not involve the usage of chemical solvents as it is a dry treatment method. In spite of the fact that corona discharge treatment increase the wettability of the surface and thus, change the chemistry of the surface which improves the adhesion, but this adhesion is not very strong which attributed to the lack on the surface roughness as this method attack the surface chemically rather than mechanically. On other hand, the chemical bonds between the surface and the plated metal are more than the mechanical bonds (Romero-Sanchez, Pastor-Blas and Martin-Martinez 2005).

1.6.6 Sonochemistry

Recently, using ultrasound through aqueous solution which is known as (Sonochemistry) has brought significant attention to the surface modification purpose (Cobley 2007a). More explanation of this subject is covered in the following chapter.

CHAPTER 2 SONOCHEMICAL SURFACE MODIFICATION

2.1 THE THEORY OF SONOCHEMISTRY

Sonochemistry can be defined as the science which describes the influence of ultrasound on chemical reactions and processes. It requires that the system irradiated with ultrasound must be a liquid which makes sonochemistry to be considered as a general activation technique such as thermochemistry which requires heating. Furthermore, sonochemistry, when compared with new chemical technologies such as microwaves, has an important advantage which is that the equipments required for this technique are comparatively inexpensive (Mason and Peters 2002: 1-2). Sonochemistry has been employed in various purposes such as: (i) general surface cleaning, (ii) water treatment to remove chemical and biological pollution, (iii) welding, cutting, soldering materials, (Mason and Peters 2002: 1-2).

Sonochemistry totally depends on the effects of ultrasound on the liquid medium. Understanding ultrasound and the ways in which it induces chemical reactions and processes is a p rime requirement. Ultrasound is described as the sound which the human ear cannot hear the sound waves have a frequency higher than the normal frequency that is audible for humans. Frequency (Hz) represents the number of sound waves that pass a fixed point in unit time (1Hz = Hertz = 1 cycle per second). While the power of ultrasound represents the intensity (volume) of the sound source (W cm^{-2}). Humans respond to sound waves with a frequency of about 16 Hz to 20 kHz and this depends on the person's age. For instance, a younger person may hear 20 kHz sound waves, whereas an older person maybe unable to respond to this frequency (Mason and Peters 2002: 3). Ultrasound has a large frequency range between 20 kHz to 500 MHz. As a result of this huge range, ultrasonic usage could be divided into two areas. Firstly, frequencies between 2 and 10 MHz are considered to have high frequency and low power (Mason and Lorimer 2002: 3). The ultrasound in this range is used in medical diagnoses (scanning), chemical analysis and physiotherapy and is called diagnostic ultrasound. The second area involves the range between 20 and 100 kH z. These have low frequencies (high power) and this area is called power ultrasound. This range is utilized in cleaning, plastic cutting, water treatment and chemical reactivity.

Ultrasound travels through a medium via inducing vibrational motion in the liquid. This vibrational motion can be visualised as the ripples on water when a stone is dropped in the water moves in cycles and molecules will revert to their normal position after the waves have passed (Mason and Peters 2002: 3). Ultrasound cannot produce chemical effects directly via an interaction between the ultrasonic waves and matter. Consequently, an indirect interaction occurs in order to produce chemical effects and this is due to a phenomenon called cavitation (see below). Since studying the chemical effects of ultrasound has increased, interest in use of ultrasound has been increased particularly in the most recent sonochemistry applications involving synthesis and modification of both inorganic and organic materials (Suslick and Price 1999).

2.2 CAVITATION AND CAVITATION THRESHOLD

Cavitation is the production and growth of microbubbles and their eventual explosive collapse in a liquid. These microbubbles are formed if a large negative pressure is applied to the liquid (Mason and Peters 2002: 6). Generally, the sound itself is a whole series of compression and rarefaction waves (see figure 2). During the rarefaction cycle, the distance between the molecules of a liquid is increased and with more of the large negative pressure produced via rarefaction cycle, the average distance between the molecules of the liquid can exceed the critical molecular distance required to hold the liquid molecules interacting with each other. At this point, the liquid breaks down and the cavitation bubbles are formed particularly when they take a small amount of vapour from solution. Cavitation threshold is defined as the point which the cavitation could be commenced and this can often be identified via a (fizzing) noise (Mason and Peters 2002: 6). The sonochemistry can be applied only at the powers above those needed to exceed the cavitation threshold.

Figure 2, Development and collapse of cavitation (Mason 1999: 10)

There are two types of cavitation. Firstly, stable cavitation where bubbles are produced at low intensities (high frequency) and which oscillate in the liquid with a lifetime of many cycles and are easy to observe with the human eye. The second type of cavitation is known as transient cavitation. These bubbles exist for a few acoustic cycles in which they grow during the rarefaction cycle and expand to at least double their initial size and then reach an unstable size. Consequently, these bubbles disappear or yield smaller bubbles which collapse violently in the compression wave (Figure2). The effect of cavitation is produced via the collapse of the transient cavitation bubbles in combination with the oscillated of stable cavitation (Mason and Peters 2002: 7).It has been reported that when this collapse occurs in the frequency of 20 kHz, a temperature up to 5000 K (4727 ^{o}C) and a pressure of 2000 atmosphere may be produced (Flint and Suslick 1991). There are two types of effects which can be induced via cavitation and these are physical and chemical effects. Below, the effects that are useful for the sonochemical surface modification will be mentioned.

2.2.1 Chemical effects

Ultrasound is known for its ability to decompose water which produces hydrogen radicals (H°) and highly reactive hydroxyl radicals (OH°) and these OH° could be considered as highly oxidising agents and reactants. These radicals are involved in subsequent reactions and eventually, a hydrogen peroxide (H_2O_2) is generated (Gale and Busnaina 1995). The generation

of these species is due to the high temperature and pressure produced via bubbles collapse. It has been disclosed that any species dissolved in the water can be subject to chemical reaction with hydrogen peroxide formed via water sonication (Mason and Peters 2002: 16).

Figure 3, Sonochemical decomposition of water (Mason and Peters 2002: 16)

The generation of radicals depends on frequency which is utilized. It has been confirmed that radical formation from water reaches a maximum at a frequency of 300 kHz (Mason and Peters 2002: 16). This means that the production of the radicals at 20 kHz will be less than the radical generation at higher frequencies. In spite of this fact, radicals that are produced at low frequency could be involved in the oxidation reaction near the surface of material. This oxidation effect cannot be omitted even if a small amount of radicals are formed using low frequency (Cai 2005). It has been mentioned in the first chapter that most of the traditional surface modification methods utilize an oxidant agent in order to attack (oxidize) the material surface. So, oxidation reactions could occur at the material surface when ultrasound is applied but not as strong as traditional surface modification treatments.

2.2.2 Physical Effects

It has been confirmed that physical effects produced via cavitation can introduce the desired material surface changes to achieve a good adhesion with subsequent electroless copper plating (Cobley, Mason and Robinson 2008). These physical effects occur primarily due to a phenomenon referred to as microjetting (Singer and Harvey, 1979). When the bubbles collapse near a material surface such as ABS plastic, epoxy resin or Noryl, the collapse becomes non-spherical with high speed liquids jets moving towards the superficies of material and this speed

could reach up to 100 m/sec (Plesset and Chapman 1971). The impingement of microjetting near the a solid surface creates a localized erosion on the exterior and this is responsible for ultrasonic cleaning, in addition to the many sonochemical effects occurring on the solid surface itself (Suslick and Price 1999). At 20 kHz frequency, the size of bubbles is bigger compared to higher frequencies so, the cavitation effect at 20 kHz would be more desirable for attacking solid surfaces as these big bubbles collapse more violently than the smallest bubbles which are produced via higher frequencies (Mason and Peter 2002: 13).

Picture (13) photo of jet formation in a collapse near a solid surface
(Mason and Peters 2002: 14)

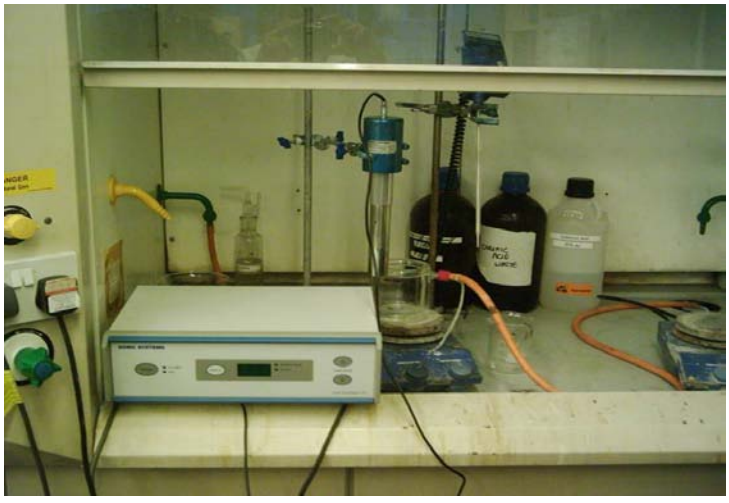
Microjetting can produce a mechanical or physical change to the solid exterior via destroying or damaging the boundary layers on the substrate surface. Theoretical work by Plesset has confirmed that the damage occurred on the solid surface was due to the liquid jet caused via sonication (Plesset and Chapman 1971). Moreover, this microjetting can increase efficiently the rate of transfer of product and reactants to and from the solid surface (Price, Keen and Clifton 1996) and for this reason, ultrasound has been used for cleaning materials in industries such as jewellery making.

2.3 ULTRASONIC EQUIPMENT

There are many commercial sources of ultrasonic power equipment. Some of these were commonly used through industry and others have been utilized for research work investigating the sonochemistry subject. Devices such as cleaning baths, whistle reactors, probe systems and submersibles could be considered as the most common ultrasonic instruments. Due to the fact that only the probe system has been employed in this project, details of other devices will be omitted.

In the probe system, the ultrasonic waves are focused in a small area which will produce more energy of ultrasound power and this is the most important reason for utilizing this type of system. The probe system consists of a horn with detachable tip, a transducer and a generator. There is variability in the probe shape such as stepped horn or linear taper horn. Most of the probes tip are replaceable due to the erosion occurred around these tips via cavitation. There are a few advantages of utilizing the probe system such as: (i) high powers up to hundreds Wcm^{-2} can be easily achieved (depending on the size of the probe unit) (Mason and Lorimer 2002: 282), (ii) tuning (which allows the minimum current to be drawn during the sonication time) of the probe system allows an optimum performance to be reached (iii) the pulse function means the reaction can be sonicated repeatedly for fraction of second which allows an adequate time for cooling between sonic pulse to be achieved.

Despite the advantages which have been mentioned above, there are also some disadvantages of the probe system which need to be mentioned such as: (i) the probe system operates at fixed frequency (most common is 20 kHz), (ii) the temperature controlling of this system is very poor particularly if a small volume of liquid and a high power is utilized, (iii) the tip of the probe can be eroded due to the cavitation influence (Mason and Lorimer 2002: 285) (In this project, a specialised type of probe horn has been used. This probe has an end which has a diameter of 27 mm which has been hard-chrome plated in order to prevent the tip, or the end of the probe, from being eroded). (iv) Using a probe means that the effects of ultrasound can be very localized.



Picture 14, Ultrasonic generator and probe

2.4 CALORIMETRY

Calorimetry is a technique which measures the energy input into a sonicated system via measuring the temperature rise of that system as a function of time and calculating the in temperature with time. The temperature measurement is implemented with a thermocouple is which placed in the reaction itself. The temperature (T) is recorded against time (t) and only takes a few minutes making this method very simple and fast for the determination of the ultrasonic power actually entering the reaction. The power in watts is calculated by the following equation (Mason and Peters 2002: 38):

$$\text{Power} = (dT/dt)c_PM \qquad \text{Equation (1)}$$

Where (dT/dt) is the initial rise in temperature which gives a parabolic curve, c_P is the heat capacity of the solvent given in J $kg^{-1}K^{-1}$ and M is the mass of solvent used (kg). If this power (Watts) is dissipated to the reaction from a probe tip which have an area measured in cm^2, then the intensity of power (Wcm^{-2}) produced by the ultrasonic source is calculated by following equation:

$$\text{Intensity} = \text{Power}/\text{Area} \qquad \text{Equation (2)}$$

Calorimetric measurement method is applied to get an approximate estimate of the ultrasonic intensity (power) or the energy density. The intensity is often reported as Wcm^{-2} and the energy density is reported as W/dm^3. The temperature of any solution under sonication is increased due to the acoustic energy absorbed via the liquid. This energy results from the incomplete conversion of ultrasonic energy from the probe which is converted into heat when it hits the solution (Mason and Peters 2002: 38). In addition with longer sonication times, it possible that the probe itself heats up because of the vibrations and this also can heat the liquid up. Increasing the temperature is also attributed to the production of the cavitation which produce high local temperatures during their collapsing.

2.5 PARAMETERS WHICH HAVE AN INFLUENCE ON CAVITATION

There are few parameters which have a great effect on cavitation. Since cavitation is necessary in order to induce sonochemical reaction, so it is essential to take these parameters into account and

have an understanding of them. With more knowledge about these factors, it is easier to arrange the experimental conditions so that the maximum effects for the sonochemical reaction can be achieved. Furthermore, reproducibility of sonochemical experiments is only achievable if these parameters have been meticulously chosen. These parameters include:

2.5.1 Frequency

It has been confirmed that frequency of ultrasound has a very significant effect on the sonochemical reaction. The amplitude (power) of irradiation is required to be increased when high frequency is applied in order to maintain the same cavitation effect in the reaction. At very high frequency, particularly at a frequency of 1MHz and more (1 MHz = 10^6 Hz), the cavitation creation becomes more difficult in the liquid. At these high frequencies, the rarefaction and compression cycles are very short and to produce cavitational bubbles, a finite time is required to create these bubbles. Therefore, at high frequency the rarefaction cycles are shorter than the time required for the liquid molecules to be torn apart which means it is almost impossible or extremely difficult to produce cavitational bubbles (Mason 1999: 11). The size of cavitation bubbles depends on the frequency. At low frequency (particularly 20 and 40 kHz), the acoustic cycles are longer so larger bubbles are produced. While at higher frequency, the acoustic cycle is short and therefore bubbles are created but with smaller size which collapse less violently. Consequently, the chemical and physical effect for the cavitation is dependent upon the frequency (Mason and Peters 2002: 8).

2.5.2 Intensity

It has been mentioned previously that to induce cavitation, the acoustic intensity must exceed the cavitation threshold value. Basically, higher intensities are required when high frequencies are utilized while at low frequencies the intensities required are lower. Increasing the intensity induces high pressure during the compression cycles which means the final bubble collapse is more violent. Consequently, more dramatic sonochemical effects are associated with higher intensities (Mason 1999: 14). However, at very high intensities a great number of cavitation bubbles are formed into the liquid. Many of these cavitation bubbles will coalesce producing larger, more long-lived bubbles and these bubbles will act as a barrier to the transfer of acoustic energy in every part of liquid so that sonochemical effects are reduced (Mason and Peters 2002:

9). In addition, cavitational bubble field near the ultrasonic horn can disrupt the passage of sound into the liquid and consequently the overall effect of cavitation is reduced.

2.5.3 Solvent viscosity

To create a cavitation bubble, a high negative pressure in the rarefaction phase is required to overcome the natural cohesive force acting within the liquid. Therefore, cavitation bubble formation should be harder in viscous liquids(Mason and Peters 2002: 10). However, the bubbles which are created in very low viscous liquids (solvents) collapse with low violence. Whilst increasing the viscosity of solutions such as water means that more energy is needed to produce cavitation, the collapse of these cavitation bubbles is very violent compared to the low viscous liquids (Mason and Peters 2002: 77).

2.5.4 Solvent vapour pressure

It has been reported that it is very difficult to produce cavitation bubbles in liquids with low vapour pressure due to the low amount of vapour which will enter the bubble (Mason 1999: 11). Furthermore, the volatile solvents or liquids which have high vapour pressure will produce cavitation bubbles at low acoustic energy and these bubbles will contain high vapour. Due to this fact, these vapour filled bubbles collapse with less violence as the collapse is cushioned by the vapour and thus cavitational effects are less compared to the liquids of low vapour pressure.

2.5.5 Temperature

The temperature of the liquid (solvent) has an important influence in the sonication reaction. Increasing the liquid temperature decreases the viscosity of the liquid as well as increasing the vapour pressure of the liquid because the molecular forces within the solvent become weaker. Thus, the cavitation threshold becomes lower which means that a lower intensity is required to produce cavitation bubbles (Mason and Lorimer 2002: 57). However, these bubbles contain more vapour pressure which will be cushioned on collapse, consequently leading to less violent collapsing and the cavitational effect is reduced. It is important to note that if a liquid is sonicated at its boiling point, large sonochemical effects are not expected to be obtained as large numbers of cavitation bubbles are produced concurrently and these bubbles will act as a barrier

to sound transmission and dampen the ultrasonic energy from the source that enters the liquid or reaction (Mason and Peters 2002: 11). Consequently, at low temperature (higher viscosity and lower vapour pressure) the collapses of the bubbles are more violent than at high temperature.

2.6 MATERIALS SURFACE TREATMENT USING ULTRASOUND

For the last few decades, ultrasound has been employed in several major manufacturing industries particularly for the purpose of surface cleaning. Ultrasonic frequencies (40-100 kHz) have been utilized to clean diverse part in industries such as aerospace, aircraft, automotive, jeweller and electronics. Materials such as ceramic, glass, plastics and rubber have been cleaned via ultrasound (Gale and Busnaina 1995). The PCB industry has utilized ultrasound to enhance the desmear processes for many years particularly using ultrasonic horizontal equipment where an improvement in the debris removal and a good level of adhesion between the substrate and the plated metal has been achieved (Kreisel and Dudik 1987). It has been demonstrated that ultrasound can enhance the adhesion between a ceramic surface and the electroless copper plating if ultrasound is utilized during the plating process (Zhao *et al.* 1995). These authors repeated that the improvement in adhesion level is achieved because the copper deposited can anchor into the fine pits on the ceramic surface produced under sonication.

It has been confirmed that ABS surfaces could be surface modified utilizing ultrasound (Zhao *et al.* 1998a). Moreover, compared to the traditional surface treatment for ABS where chromic acid is used, ultrasonic treatment using water has been reported to show better results particularly in terms of more uniform microcavities which are produced at the surface of the ABS due to the microjetting influence caused by ultrasound (Zhao *et al.* 1998a). These microcavities on the ABS surface have played an important factor in producing good adhesion between the surface and subsequent electroless copper plating as it was described in chapter (1). The chemistry of the surface has been changed as particular groups such as carboxylic acid and aldehyde groups have been produced on the ABS surface. It has been indicated previously that the chemical bonds can play a significant part in improving the adhesion between the surface of material and the electroless copper plating. A 28 kHz ultrasonic probe was used in Zhao *et al.* (1998a) work which produces less amount of radicals than higher frequencies. However the radicals ($OH^{\bullet}$) which formed via ultrasound react more effectively with polybutadiene copolymer and produced

groups such as carboxylic acids and aldehyde on the ABS surface (Zhao *et al.* 1998a). These groups increase the chemical bonds between the substrate and the electroless metal plating. The surface roughness also has been increased.

Similar results have been achieved when ultrasound has been used to surface modify PVC plastic. Work done by Zhao *et al.* (1998b) indicated that a PVC (Polyvinyl Chloride) plastic could be surface modified via applying ultrasound. A 28 kHz ultrasonic probe has been used in their work at optimum temperature of 29 ºC. It has been confirmed that employing a solvent with less vapour pressure such as acetone is more effective than employing a solvent with high vapour pressure such as alcohol in a sonochemical reaction. This is because the solvents with very high vapour pressure produce vapour filled bubbles whose collapse is cushioned and therefore less violent collapse occurs (Mason 1999: 11). The time of the sonication has been shown to be an important influence in PVC surface treatment as a good level of surface roughness is achieved when more treatment time has been utilized. It has been confirmed that radicals are produced utilizing 28 kHz ultrasonic probe in order to surface modify PVC, this was proved by monitoring the formation of carboxylic acid groups (Zhao *et al.* 1998b). Furthermore, it was suggested that the radicals ($OH^{\cdot}$) which are formed via water sonication react with C─H or C─Cl bonds and form alkoxyl radicals which further decompose into organics groups such as carboxylic acids and aldehyde. Carboxylic groups were the same as the groups which were produced when the PVC was treated by traditional surface modification processes using chromic acid (Zhao *et al.* 1998b). In Zhao *et al.* (1998b) work, The surface roughness for PVC has shown an increase as more and larger microcavities were produced on the surface via using ultrasound.

It has been confirmed that a thin layer of polar groups such as carbonyl groups including carboxylic and/or ester groups have been formed on the surface of polyethylene polymer (Price, Clifton and Keen 1996) using an ultrasonic probe at intensity of 32 Wcm^{-2} at 35 °C temperature. The formation of these groups are attributed to the generation of hydroxyl radical species produced by sonication processes which can be reacted further with the polymer surface to give carboxylic and/or ester groups on extended reaction. Moreover, it has been confirmed that by using persulfate oxidizing agent with ultrasound, the oxidation of the polymer surface can be increased. This was demonstrated via contact angle measurement for the tested polymer (polyethylene) and the surface modification was improved (Price, Keen and Clifton 1996).

Hydrogen peroxide was also used and has shown an influence on increasing the surface modification rate compared to traditional methods using chromic acid. It has been claimed that using an oxidizing agent such as persulfate is more effective than using hydrogen peroxide as an oxidizing agent (Price, Keen and Clifton 1996). Hence, potassium persulfate showed an increase in the decomposition rate of water under sonication which accelerated the generation of radicals caused via ultrasound.

More recently, ceramic material has been claimed to be effectively surface modified using ultrasound (Cobley, Mason and Robinson 2008). The surface roughness of the ceramic was increased, which means that a physical change occurred on the surface. This physical erosion of the surface was considered by these authors to be due to the microjetting effect rather than any chemical effect which is usually attributed to radical formation during sonication. Epoxy material (high Tg) has been successfully surface modified by employing ultrasound as the roughness of the surface and the adhesion level were increased at the surface (Paniwnyk and Cobley 2010)

The surface of noryl material has been treated using ultrasound and it has been shown that a good level of surface modification could be achieved after ultrasonic treatment was applied utilizing an ultrasonic probe at 20 kHz at 40 ^{o}C for 60 minutes (Cobley and Mason 2007). The roughness and weight loss measurements have indicated that noryl surface was significantly changed via ultrasound (see Pictures 15 and 16) while the contact angle measurement indicated that there is some alteration in the chemistry of surface, but this is not as effective for the surface modification as the physical effect (roughness).

Picture 15, Noryl surface as received (Cobley and Mason 2007)

Picture 16, Noryl surface after ultrasonic treatment (Cobley and Mason 2007)

2.7 SURFACE ANALYSIS TECHNOLOGIES

There are a number of surface analysis methods which have been employed into this project in order to confirm any changes that have been occurred on the material surface after surface modification under sonication processes. The purpose behind employing several types of surface analysis methods is to obtain as much information as possible about the changes produced at the surface. A brief description about each method is shown as follows:

2.7.1 Weight loss

This is a quick and simple method to determine the amount of any material that has been removed from the surface via ultrasound treatment. It has been mentioned that most of traditional and alternative surface modifications methods are utilizing an etchant process which means that if successful, the treated substrate loses some of its weight due to the removal of some of surface material. This method gives an indication about any changes that happen and about the efficiency of the technology which is used to surface modify material. It has been confirmed that the microjetting generated via ultrasound can remove some part of the surface and this is described as weight loss (Gale and Busnaina, 1995). This method has been used via many researchers such as Cobley and Mason (2007) and Zhao *et al.* (1998a).

2.7.2 Contact angle

The contact angle measurement can be defined as the contact angle which is results from the interface between a liquid and solid. It is used particularly in order to evaluate the polymer wettability as a function of surface modification (Ge, Turunen and Kivilahti 2003). The wettability of any polymer depends on the state of the surface such as the roughness and the chemistry of the material surface. Actually, the prime change in the surface chemistry is to increase the hydrophilic nature of the surface which has been shown to be an important factor in producing good adhesion between the substrate and the electroless copper plating (Soubestre and Khera, 1971). The contact angle measurement can also be used as an indicator about the surface energy of the material surface. Figure (4) shows the relationship between the contact angle and the wettability, adhesion and surface free energy.

Figure (4) Relation between the contact angle and others surface properties
(Kyowr n.d.)

2.7.3 Roughness

Roughness measurement is used to determine the texture of the surface. Generally, if the surface modification processes is applied to treat any material, the surface of that material will become rougher which causes the subsequent electroless plating to be anchored to the surface of the material. The rough surface produced via ultrasound is believed to be due to the microjetting effect of the cavitational bubbles collapse near the surface which erodes it. Consequently, this type of surface analysis has been utilized by many researchers such as Zhao *et al.* (1998a), Cobley and Mason (2007) and it gives an indication about the surface properties after treatment.

2.7.4 Gloss meter %

The gloss meter is an instrument (see Picture 20) which can measure the reflective qualities of the manufactured surfaces via applying a light with known intensity at the material surface and measuring the reflective light (DMV-UK 2009). It could be an indicator to confirm any physical change (roughness) occurring at the surface of material after treatment as it will measure the smoothness of the surface. A high reading of gloss meter means the surface reflects more light and this indicates for a smooth surface while a lower reading indicates for a rough surface which reflects less value of light.

Picture 17, Stargloss Glossmeter (Caltech Engineering Services 2009)

2.7.5 Scanning Electronic Microscope (SEM)

The SEM is a microscope that utilizes electrons rather than light to generate an image. It can produce images of high resolution which means that closely spaced features can be examined at high magnification e.g. (indicates level required) (Anon n.d.). There are several advantages for using SEM such as: (i) it can give larger depth of focus of the sample surface, (ii) greater resolution and high magnification and this can be attributed to the very narrow electron beam utilized in this instrument which can produce a large depth of field yielding a ch aracteristic three-dimensional appearance which is very useful to understand the surface topography of the tested samples, (iii) it is easy to observe the samples a long as the samples are conductive. These advantages have rendered this instrument to be widely used in the research area particularly in the surface modification field via many researchers such as Mandish (1994), Cobley and Mason (2008).

2.7.6 Adhesion test

The adhesion test is performed to assess the level of the adhesion between the surface and the subsequent electroless copper plating. The type of adhesion test employed in this project is known in the trade as the (Scotch Tape Test) which is widely adopted in industry (Teixeira and Santini 2005). Samples from the material which have been surface modified were electroless copper plated in order to determine the adhesion level. The procedure has been described in 3.10.7. Currently, there is no instrument to measure the adhesion level. As the adhesion measurement was assessed visually makes this measurement a qualitative method.

2.8 ATOMIC FORCE MICROSCOPY (AFM)

AFM (Atomic Force Microscope) is another type of microscope which was first used in 1986 by Gerd Binning (Group 2004). It is an instrument which can examine the surface of the sample and make a measurement in three-dimensions via measuring the forces between a sharp tip (which is generally a couple of microns long and often less than 100Å in diameter) and the surface at a very short distance (Robert and Heather n.d.). Thus, the image of the sample surface is presented in three-dimensions. This means that that the surface characteristics can be observed with very accurate resolution ranging from 100 μm to less than 1 μm. It operates a sharp tip which is made either of silicon or Si_3N_4 and attached to a constant cantilever (Blanchard 1996) and moves over the surface and scans the surface of the sample. Either the actual tip deflection or the repulsive force between the tip and sample is recorded relatively to spatial variation which then converted to an image of sample surface (Group 2004). A semiconductor diode laser is bounced off the back of the cantilever onto a position sensitive photodiode detector. This detector measures the bending of the cantilever while the tip is scanned over the surface. The measured cantilever deflections are used in order to create a map of the sample surface topography and generate a three-dimension image. This instrument has been used by several researchers such as Yang *at al.* (2009) and Kim *at al.* (2006) in order to generate images for surface analysis purpose. Using this can give a close idea about the mechanical bonds between the surface and the plated metal as it generates a three-dimension image for this surface. Unfortunately, this instrument is not available to be used at Coventry University. So SEM was the only instrument utilized to get pictures in order to analyse the surface of the tested materials.

CHAPTER 3 EXPERIMENTAL

3.1 MATERIALS

The following materials were utilized in this project:

1) Noryl (HM4025) Polyphenylene ether – polystyrene (supplied by Sabic).
2) Epoxy Tg resin (Isola 370HR) (Supplied by Isola).
3) ABS (Cycolac S705) – Acrylonitrile Butadiene Styrene (supplied by Sabic).
4) Ceramic material (Zirconium Tin Titanate) supplied by Morgan Ceramics.

3.2 CHEMICALS

The solvents mixtures which were utilized in the project were:

1) NMP, 1-Methyl-2-Pyrrolidinone, 99+% Reagent (C_5H_9NO) was purchased from Sigma Aldrich. NMP mixture was prepared by adding 5 % by volume of NMP to 200 ml of DI water.
2) Ethylene glycol, Reagent plus >=99%, $C_2H_4(OH)_2$ was purchased from Sigma Aldrich. Ethylene glycol mixture was prepared by adding 5 % by volume of Ethylene glycol to 200 ml of DI water.
3) Butyl carbitol, Diethylene glycol butyl ether Reagent plus > 99%, $C_8H_{18}O_3$ was purchased from Sigma Aldrich. Butyl carbitol mixture was prepared by adding 5 % by volume of Butyl carbitol to 200 ml of DI water.
4) Gamma-Caprolactone 98%, $C_6H_{10}O_2$ was purchased from Sigma Aldrich. Gamma-Caprolactone mixture was prepared by adding 5 % by volume of Gamma-Caprolactone to 200 ml of DI water.

3.3 EQUIPMENTS

1) Sonic system frequency 20 kHz (Sonic processor P100).
2) Four figure balance BDH (AA-250) weight was used to calculate the weight loss.
3) Oven (Heraeus instruments) was used to dry the samples before and after treatment.
4) Timer (Fisher scientific) was employed to monitor the sonication time.
5) Thermometer (Digitron instrumentation 3208 K) used to observe the sonication temperature.

6) Cooling system (40 to -20 ºC) Julabo FL300. This instrument was utilized to enable the low temperature experiments to be performed.
7) A Kruss D100 contact angle measuring system used to do the contact angle measurements
8) The Rank Taylor Hobson Form Talysurf 120L utilized equipment for roughness analysis method.
9) A Stargloss Glossmeter at 60º for Gloss meter measurement.
10) A Jeol JSM-6060LV Scanning Electronic Microscopy. This instrument was employed to analysis the surface and get a close pictures.

3.4 DETERMINATION OF THE ACOUSTIC POWER

Calorimetric method of power determination

200 ml of de-ionised (DI) water was placed inside a 250 ml glass beaker. The ultrasonic probe was placed 1 cm above the bottom of the beaker (this position was utilized for all the experiments). Sonication was applied and the temperature rise was recorded with a thermocouple which was immersed in the vessel (in the same position for all the experiments). All the experiments were performed at 40 ºC. When the ultrasonic probe was turned on, the temperature reading was taken every 5 seconds for first minute, 10 seconds for the second minute and 20 seconds for third minute. The temperature was then plotted versus time using a third degree polynomial which was then used to determine dT/dt. The power (W) and then the ultrasonic intensity (Wcm^{-2}) were calculated for each experiment utilizing the equations 1 and 2.

$$\text{Power} = (dT/dt)c_PM \qquad \text{Equation (1)}$$

$$\text{Intensity} = \text{Power}/\text{Area} \qquad \text{Equation (2)}$$

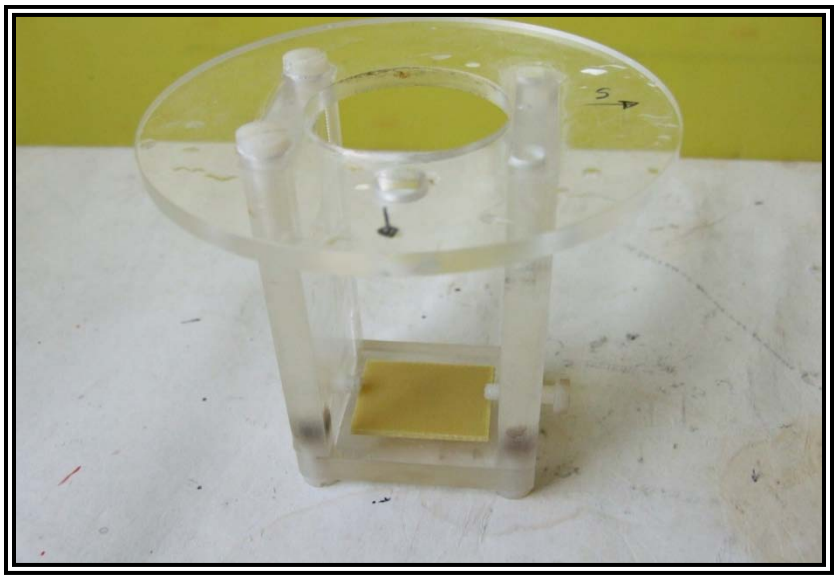
The above experiment was repeated utilizing ultrasonic power settings of 10 W, 25 W, 50 W, 80 W and 100 W. All the experiments were performed in three replicates (for each individual power) and the average reading was taken. The calorimetric experiment was also performed at a low temperature of 0 ºC (by using Cooling system Julabo FL300) using powers of 50 W and 80 W.

3.5 SAMPLE PREPARATION

All samples Noryl, ABS, Epoxy Tg resin and Ceramic material were cut into pieces with dimensions approximating 2.5 cm x 3.0 cm. The samples were cleaned with ethanol. To weigh the samples before treatment with ultrasound, samples were rinsed in tap water for 5 minutes and then in DI water for 2 minutes. The samples were placed in the oven at 90 ºC for 1 hour and moved to the desiccator for 1 hour to return to room temperature. Then the samples were placed again in the oven at 90 ºC but for 30 minutes and placed in the desiccator for 30 minutes to make sure that all humidity had been removed and to obtain a constant weight (g). The samples were then reweighed to 4 decimal places

3.6 GENERAL SONOCHEMICAL SURFACE MODIFICATION PROCESS

The prepared samples of Noryl, Epoxy (Tg resin), ABS and Ceramic material were placed in a purpose-built holder which was designed as shown below (Picture 18). This holder was utilized in order to make sure that the samples were held securely during the treatment.



Picture (18) Samples holder

The sample holder was then placed into a water jacket flask where 200 ml of DI water was added to it see Picture (19) below. The 20 kHz ultrasonic probe was located 1cm above the samples for all the experiments. The samples were then sonicated for 15 minutes (this period was utilized for all the experiments) at 10 W and the solution temperature was monitored using the thermocouple

but maintained at 40 ºC. The experiments for each material were performed in five replicates and the average reading was taken. After treatment the samples were analysed using the techniques described in 3.11.

For the control experiment, the above experiment was repeated in the absence of sonication and the solution was stirred by a stirrer. The experiments for each type of tested material were performed in three replicates and the average reading was taken. After treatment, the analysis methods in section 3.11. were carried out for the samples.

Picture (19) Water jacket

3.7 THE OPTIMIZATION OF POWER SETTING FOR SONOCHEMICAL SURFACE MODIFICATION

The experiments above were repeated for the prepared samples (Noryl, Isola, ABS and Ceramic) were sonicated for 15 minutes at 25 W, 50 W, 80 W and 100 W. The experiments for each material were performed in five replicates for each individual power (W) and the average reading was taken. The optimal sonication power for each material was identified at 40 ºC and after treatment the samples were analysed using the techniques described in section 3.11.

3.8 EFFECT OF TEMPERATURE

The general sonochemical surface modification experiments see section 3.6. were repeated but utilizing only the optimal power setting previously determined for each individual material (80 W for Isola, ABS and Ceramic) and 50 W for Noryl. In addition the Isola, ABS and Ceramic samples were also sonicated at 50 W for comparison purposes. In these cases experiments were performed at temperatures approximating 0 ºC by using cooling system Julabo FL300. The experiments for each material were also performed in five replicates and the average reading was taken. After treatment, the samples were analysed.

3.9 EFFECT OF FREEZING SAMPLES PRIOR TO SONICATION

The prepared samples were placed in a freezer for 24 hours. The samples were then treated as previously described in section 3.6 with sonication at 50 W at temperatures approximating 0 ºC using cooling system Julabo FL300 and then also at 40 ºC. The experiments for each material were performed in five replicates and the average reading was taken. After treatment, the samples were analysed.

3.10 EFFECT OF ADDING SOLVENTS ON THE SONOCHMEICAL SURFACE MODIFICATION

Solvent mixtures used to treat the samples were prepared by adding 5 % by volume of each solvent (NMP, Ethylene glycol, Butyl carbitol and Gamma-Caprolacton) to 200 ml of DI water. The general sonochemical surface modification process was then performed in each solvent mixture at 50W and at temperatures approximating 0 ºC. The experiments for each material were performed in five replicates for each individual solvent solution and the average reading was taken. After treatment, the analysis methods were carried out for the samples.

For the control experiment, the above experiment was repeated in the absence of sonication and the solution was stirred by a stirrer. The experiments for each material were performed in five replicates and the average reading was taken. After treatment, the analysis methods were carried out for the samples.

3.11 SAMPLE ANALYSIS METHODS

Several analysis methods were utilised for most of samples except for the Ceramic material samples. Due to the fact that the shape of the Ceramic is cylindrical, it was not possible to carry out two of the analysis methods namely the contact angle test and the gloss % test. The analysis methods were as follows;

3.11.1 Weight loss

Weight loss is a simple method of calculating surface removal from materials. The weight of each sample was recorded before the treatments as described in section 3.4. and the weight for each sample was recorded following the same processes;

1. The samples were rinsed in tap water for 5 minutes and then in DI water for 2 minutes
2. Dried in the oven at 90 ºC for 1 hour.
3. Stand in the desiccator for 1 hour to return to room temperature.
4. Repeat steps 2 and 3 for 30 minutes in order to achieve constant weight (g)
5. Weigh the samples to 4 decimal places

The amount of weight loss was calculated as follows;

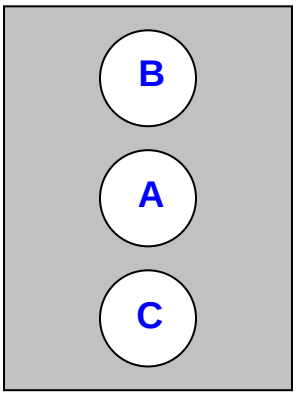
$$\text{Weight loss (g)} = \text{Weight before treatment (g)} - \text{Weight after treatment (g)} \quad \text{Eq (3)}$$

$$\text{Weight loss (mg/cm}^2\text{)} = \text{Weight loss (g)} \times 1000 / \text{Area (cm}^2\text{)} \quad \text{Eq (4)}$$

This equation was used to calculate the ratio of weight loss according to the area of each sample.

3.11.2 Contact angle

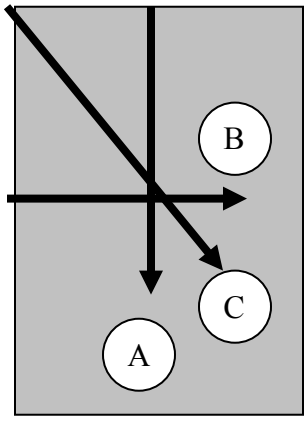
This analysis technique was utilized to measure the contact made between a drop of liquid (e.g. water) and the surface of material. A Kruss D100 contact angle measuring system was utilized for this analysis method. The measurement was performed via taking three reading from different location for each sample as follows:



As (A, B and C) refers to the three different locations. The average of three measurements was calculated. The lowest contact angle refers to high wettability which suggests a high surface energy and this might be lead to good adhesion of the coating to the substrate.

3.11.3 Roughness

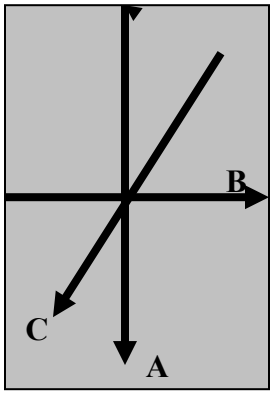
The Rank Taylor Hobson Form Talysurf 120L equipment was utilized for this analysis method. The roughness for each sample was calculated over a 1.3 cm length of the surface of each material. This operates with a co ntact stylus moving across the surface of the sample and roughness is measured using a laser interferometer. The software calculates roughness as an Ra value i.e. the arithmetic departure of the roughness profile from the mean line µm. Three reading were taken for each sample from different locations as follows;



As (A, B and C) refers to the three different locations. Then the average for three reading was calculated.

3.11.4 Determine of Gloss Meter %

The device which was utilized in this method was a Stargloss Glossmeter at 60º. A high reading (reflectance of more light) suggests a smooth surface whilst a low reading (reflectance of less light) refers to a rough surface. The measurement was performed via taking three readings from different locations for each sample as follows:



As (A, B and C) refers to the three different locations. Then the average for three reading was calculated.

3.11.5 SEM

After surface treatment, samples from each material were-sputter coated with palladium/gold via utilizing a sputter coating apparatus (Quorum Technologies). As result of this step, a thin layer of palladium/gold was deposited on the surface of material to enable SEM analysis. Then samples were tested using a Jeol JSM-6060LV SEM. A photograph was taken at particular magnification depending on the tested material. Then the texture of the surface was assigned by grading the photograph from 0-10 indication for the texture level of the surface (0 indicates to low level of texture (eg. smooth surface) while 10 indicates to high level of texture (eg. extreme change in surface morphology). On the other hand, the pictures were assessed according to texture level (roughness level) and the cavities that formed at the surface after treatment. An example scale to show how the pictures were assessed visually for epoxy (Tg resin) is shown as follows:

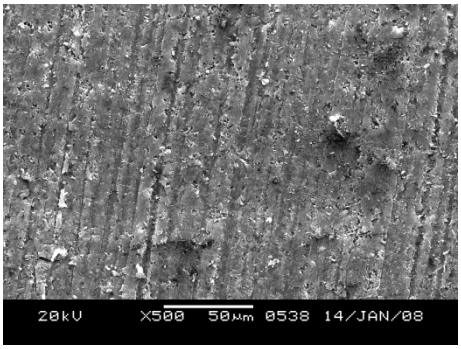
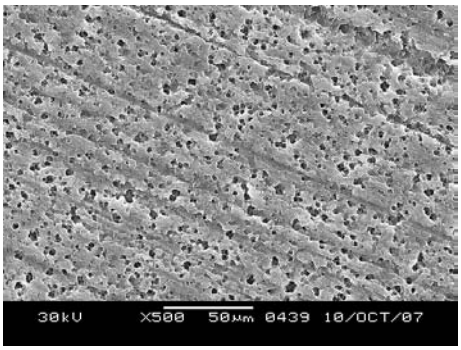
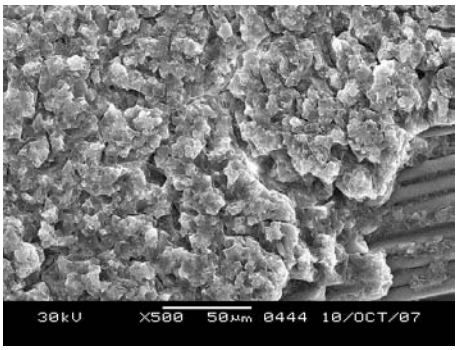
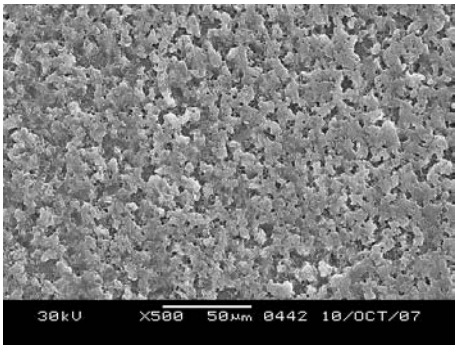
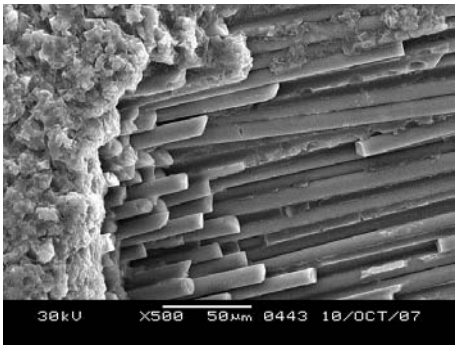
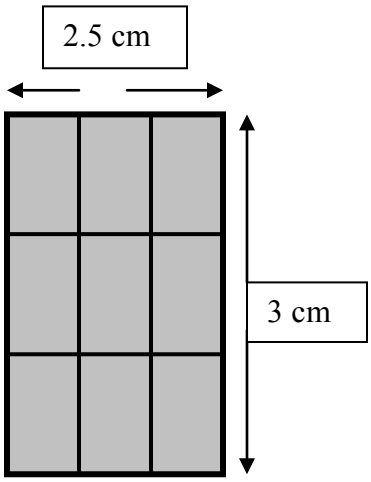
Picture Grade (0-10)	Picture as shown by SEM	Picture Grade (0-10)	Picture as shown by SEM
0 (As received)	 **a fairly smooth surface**	**6**	 **some exposure of glass fibres**
2	 **some pitting of the surface is observed**	**8**	 **further deepening of pitting plus more fibre exposure and change in morphology of epoxy**
4	 **deeper more extensive pitting**	**10**	 **extensive fibre exposure**

Table 1, Epoxy (high Tg) SEM pictures level scale

3.11.6 Adhesion

The ultimate reason for carrying out surface modification on these substrates is to improve the degree of adhesion and for this reason, the treated samples were electroless copper plated see section 3.12., and then the tape test (Cobley and Mason, 2007) was utilized to determine the bond strength (adhesion) between the coat and the substrate. A cross-hatch grid was cut into the surface of the test sample using a sharp tool as follows:



The tape (sell tape) then was applied to the surface of the samples and pulled from the surface firmly. All samples were graded qualitatively from 0-10. These numbers indicates to the electroless copper plating level that have been adhered to the surface. On other hand, the adhesion level is graded according to the copper plating level of each single grid (see above figure) which remained after the tape had been pulled from the surface. Grade 10 indicates to good adhesion (no electroless copper was removed) while 0 grade indicates that the entire coat was removed.

There is another type adhesion test which employed by the researchers and the electronic industries which is known as peel strength measurements (Siau *et al.* 2004c). After the surface has been copper plated, the force which is necessary to peel the copper off the surface is recorded by peel strength measurements instrument and this force gives an indication about the adhesion strength between the polymer surface and the plated copper. Currently, this instrument is not available at Coventry University.

3.12 METALLIZATION PROCESSES

All of the samples from various materials tested have been electroless copper plated in order to determine the adhesion for them except one sample from each experimental sample group run which was sputter coated to prepare it for the SEM analysis. The metallization products are originally prepared and called as Rohm and Haas and they were supplied by Chestech in UK. Metallization processes for the samples were as follows:

1- The samples were immersed in Circuposit Conditioner 3323 at 50 °C for 3 minutes and water rinse for 3 minutes followed by another water rinse for 3 minutes but in different beaker.
2- The samples were immersed in Cicuposit Pre-dip 3340 RT for 1 minute.
3- The samples were immersed in Circuposit Catalyst 3344 (3%) 40 °C for 5 minutes and Water rinse for 2 minutes followed by another water rinse for 2 minutes in different beaker.
4- The samples were immersed in Cicuposit Electroless Copper (3361) solution at 30 ºC for 20 minutes then to water rinse for2 minutes followed by DI water rinse for 2 minutes.
5- Finally, samples were placed in the Oven at 90 ºC for 1 ho

CHAPTER 4 RESULTS AND DISCUSSION

4.1 CALORIMETRY.

Calorimetry is a quantitative measurement of the heat involved in a chemical reaction to estimate the actual power entering into the reaction. In this project, the calorimetry measurement has been used to determine the ultrasonic intensity (Wcm^{-2}) under two different temperature conditions which are described as following:

4.1.1 Calorimetry for optimization of powers

In this part calorimetry has been utilized to determine the ultrasonic intensity (Wcm^{-2}) for the 20 kHz ultrasonic probe at different power settings in water at 40 ºC as it was described in section 3.3. After the measurement, the equations 1 and 2 have been used to calculate the ultrasonic intensity (Wcm^{-2}). The results are tabulated as follows:

$$\text{Power} = (dT/dt)c_P M \qquad \text{Equation (1)}$$

$$\text{Intensity} = \text{Power}/\ \text{Area (Surface of probe)} \qquad \text{Equation (2)}$$

The results are tabulated as follows:

Power setting	Power by calorimetry (W)			Mean Power (W)	Ultrasonic Intensity (Wcm^{-2})
	Run (1)	Run (2)	Run (3)		
10	10.8	10.4	11.3	10.8	**1.3**
25	19.1	21.2	24.3	21.5	**2.7**
50	37.9	39.0	38.5	38.5	**4.8**
80	64.2	68.4	66.7	66.4	**8.3**
100	82.4	89.2	92.9	88.2	**11.0**

Table (2) Calorimetry for different power settings at 40 ºC

Table (2) shows the calorimetry measurement for different power settings (10 W, 25 W, 50 W, 80 W and 100 W) at 40 ºC. The results obtained clearly indicate that by increasing the power setting of the 20 kHz ultrasonic probe, more ultrasonic intensity is generated. At 10 W the ultrasonic intensity was 1.3 Wcm^{-2} which was the lowest intensity generated while the highest ultrasonic intensity was 11.0 Wcm^{-2} obtained when a 100 W setting was utilized. Ultrasonic intensity increases as the power is increased because more acoustic energy is absorbed via the liquid which means that more heat is generated in the liquid (Mason and Peters 2002: 9).

4.1.2 Calorimetry at lower temperature

The calorimetry experiment was repeated as previously described but at a lower temperature (approximately 0 ºC (see section 3.3)). Power settings of 50 W and 80 W were examined at this temperature and the ultrasonic intensity was calculated using equations (1) and (2) mentioned

above. The reason for choosing these powers will be explained later. The results obtained were tabulated as following:

Power setting	Power by calorimetry (W)			Mean Power (W)	Ultrasonic Intensity (Wcm^{-2})
	Run (1)	Run(2)	Run(3)		
50	46.0	43.5	46.8	45.4	**5.7**
80	61.8	62.7	64.3	62.9	**7.8**

Table 3, Calorimetry for power settings of 50W and 80 W at Low temperature (0 ºC)

Table 3 shows clear evidence that by lowering the water temperature, the ultrasonic intensity using a power setting of 50 W at 0 °C (5.7 Wcm^{-2}) is somewhat higher compared to the same power setting at 40 °C (4.8 Wcm^{-2}). The reason is, at low temperature the molecular forces within the liquid become stronger which means that the cavitation effect will be more (Mason and Peters, 2002: 11). When the power setting was 80 W, the results indicate that a slightly higher ultrasonic intensity was obtained at 40 ºC rather than the lower temperature. Although there is a very little difference between the values, this difference could be attributed to the fact that at a lower temperature, the cavitation effect can be increased but with more power the cavitation bubbles will coalesce producing larger, more long-lived bubbles and these bubbles will act as a barrier to the transfer of acoustic energy in every part of liquid (Mason and Peters, 2002: 11).

4.2 EPOXY (HIGH Tg RESIN) SONOCHEMICAL SURFACE MODIFICATION

Epoxy (high Tg) resin material is used widely in printed circuit boards (PCB) manufacturing. Different kinds of surface modification processes have been successfully employed to change the surface properties so a good level of adhesion could be achieved between the material surface

and the subsequent electroless plating (Jawitz, 1997). Among many processes employed that of a solvent swell followed by alkaline permanganate (commonly known as swell and etch) is the most accepted and applied process which is used nowadays in the electronics industries (Goosey and Pool 2004). Recently, ultrasound has been reported to have an ability to surface modify this type of laminate (Cobley 2007a). In this project, a few parameters (such as an optimum power setting, using low temperature and examine the effecting of adding solvents) have been examined to enhance the ultrasonic effect on the surface of this material.

Samples (coupons) of epoxy (high Tg) resin were analysed for surface modification purpose via several methods in order to establish a base line value which the ultrasonic treatment results could be compared to. All the coupons were immersed in DI water for 15 minutes at 40 ºC and then all the analysis methods described in section 3.11 were utilized. The combined results of all the diagnostic tests conducted for this purpose can be seen in the Table 4 as follows and are the average values of three repeat tests:

Weight loss (mg/cm^2)	Contact angle (θ)	Roughness (µm)	Gloss Meter %	Adhesion (Grade)	SEM (texture) (Grade)
0.0441	**85.7**	**0.3595**	**3.1**	**6.0**	**0.0**

Table 4, Base line value results for Epoxy (high Tg) resin surface modification tests

4.2.1 The optimization of power setting for sonochemical surface modification using Epoxy material.

Experiments were carried out to determine the optimum power setting which could be useful for this purpose in the following experiments. The results obtained are shown as following:

A- Weight loss

Figure 5 shows the weight loss recorded at different power setting for the epoxy material. The higher the recorded weight loss, the more material is removed. The results were as follows:

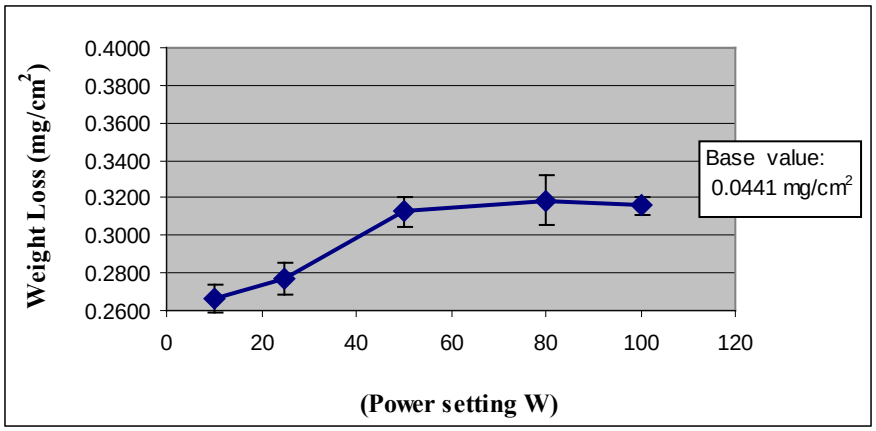


Figure (5) Weight loss for Epoxy (high Tg) resin at different power settings

Results indicates that weight loss increases up to an applied power setting of 80 W and then the level slightly decreases at the power setting of 100 W. It is obvious that the 50 W setting could produce similar values of weight loss to the 80 W setting.

B- Contact angle

The contact angle measurements at different power settings for ultrasound treatment for epoxy (high Tg) resin are shown in Figure 6 (below). A lower contact angle value suggests that there are chemical changes occurring at the surface and more wettability is produced, indicating for surface modification.

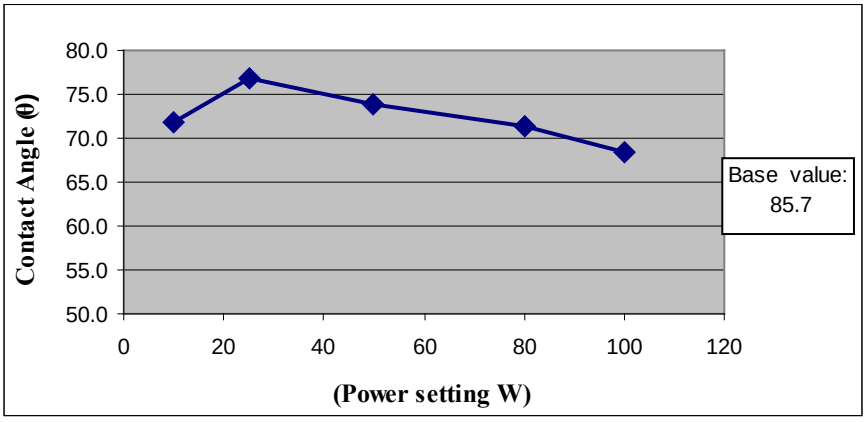


Figure (6) Contact angle for Epoxy (high Tg) resin at different power settings

Initially, the results shows that contact angle increases at the 25 W power setting and then values decrease as the ultrasonic power setting is further increased, meaning that greater surface chemistry changes occurs at higher power settings.

C- Roughness

Roughness determination following ultrasonic treatment has been carried out. Roughness analysis data for epoxy at different power settings are shown in Figure 7. Higher readings suggesting that the surface is more roughened and more surface topography is obtained

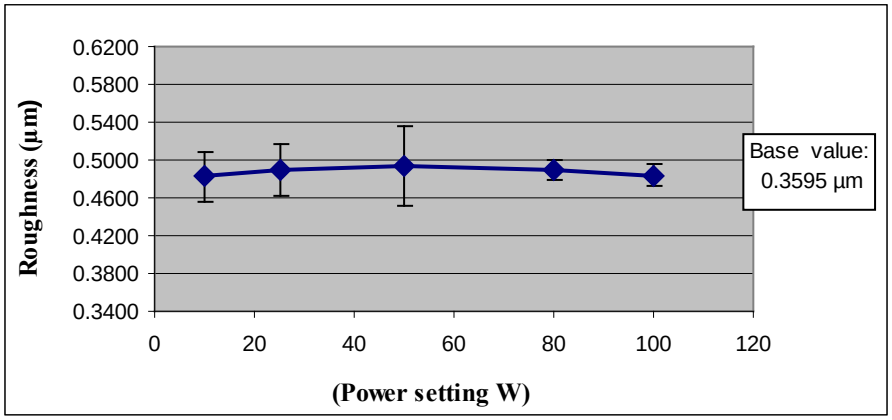


Figure (7) Roughness measurements for epoxy (high Tg) resin at different power settings

In spite of this fact that the roughness values obtained at different power settings were very close to each other, the results in Figure 7 show that the roughness increases slightly at 50 W and then level out at 80 W and 100 W. All ultrasonic treatment provided an increased roughness compared to the initial base value.

D- Gloss meter readings

The gloss meter results for epoxy at different power settings are shown in Figure 8, the lower the values indicating that the surface is less smooth (more roughness), pointing to some surface modification having occurred at this point in time. The results are shown as follows:

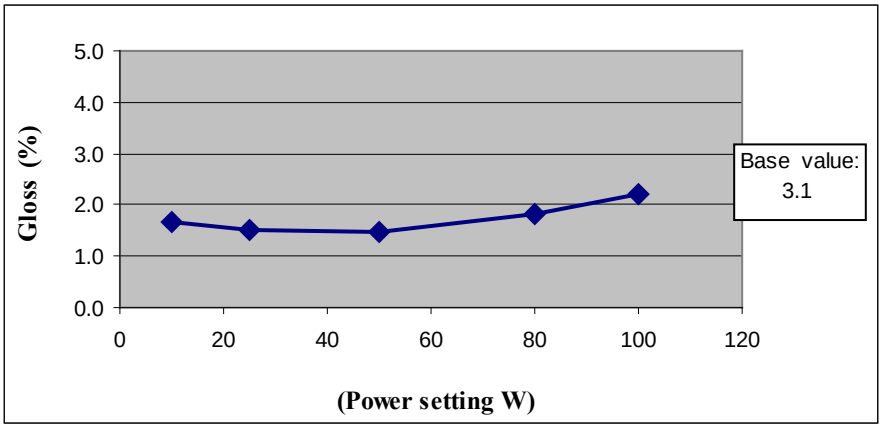


Figure (8) Gloss meter readings for Epoxy (high Tg) resin at different power settings

It should be noted that all values for the gloss meter readings were very low but, taken into consideration; the results indicate that the minimum value for gloss meter occurs at 50 W which was almost the same at 25 W. This means that higher power settings are not necessarily required to produce greater surface modification. The values increase when power settings were further increased.

E- Adhesion (Grade)

The adhesion level has been assessed at each power setting qualitatively and the results determined according to the units from 0-10 and are shown below. The high value (10) means good adhesion has been achieved. The results are shown in Figure 9.

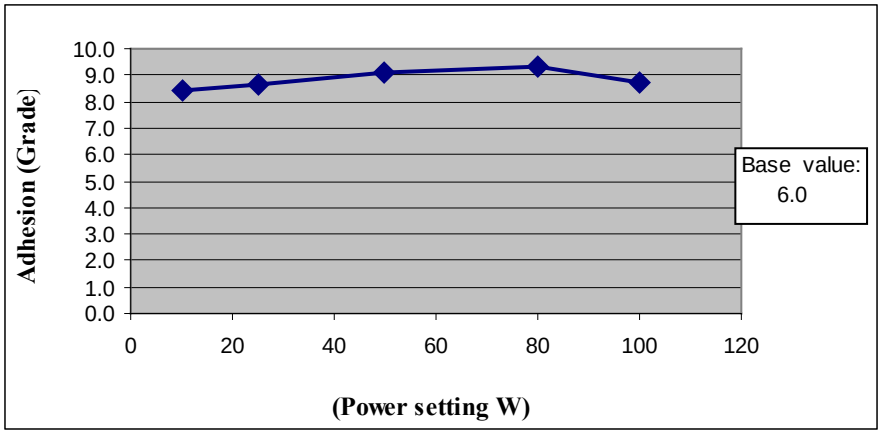


Figure (9) Adhesion grade for Epoxy (high Tg) resin at different power settings

Figure 9 indicate that the adhesion partly increase compared to base line data with increasing the power settings up to a value of 80 W. Above this value, the adhesion slightly drops. Consequently, the highest adhesion level achieved at 50 W and 80 W power settings, while the highest power setting of 100 W produced low adhesion level.

F- SEM Pictures (Grade)

Scanning electron microscope pictures have been visually assessed and each picture has been given a grade from 0-to 10. The higher value refers to good texture at the surface. In addition, the pictures showing the highest texturing are also included (Picture 21 and 22). The results are shown in Figure 10 below.

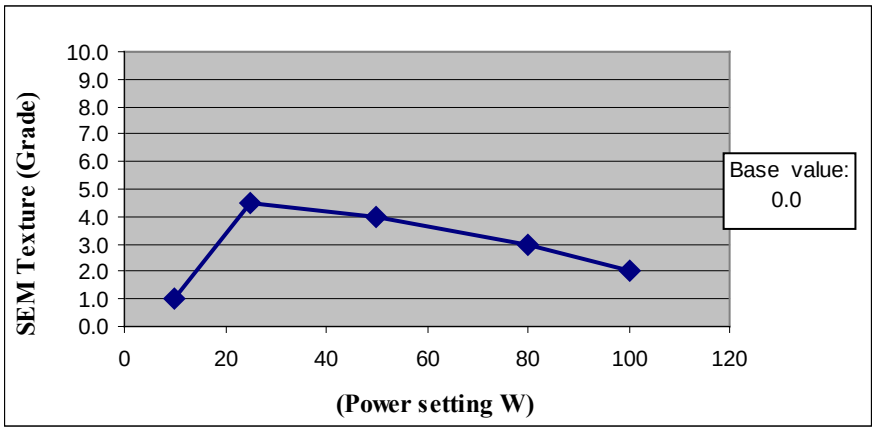
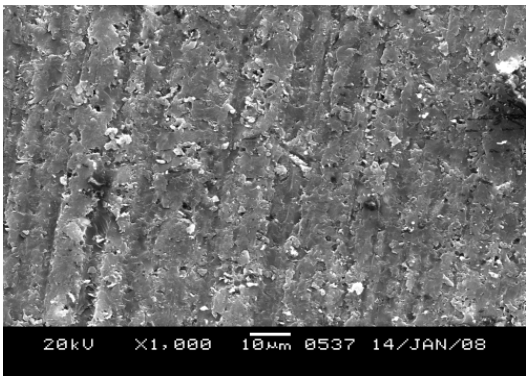


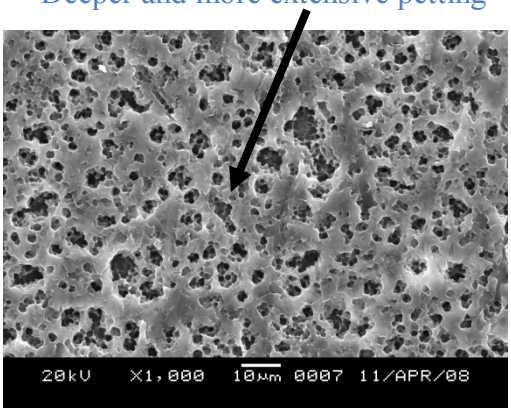
Figure (10) SEM Pictures grade for Epoxy (high Tg) resin at different power settings

Figure 10 shows the SEM texture grade initially increases with increased power setting up to a value of 25 W. thereafter, the value drops. Pictures (21 and 22) show the surface morphology of the epoxy at power settings of 25 W and 50 W. In these pictures, the pitting on the epoxy surface are clear while the untreated epoxy surface showed less surface texture (Picture 20). It must be taken into account that the surface morphology at 25 W shows a slight clearer etched surface than the samples treated using the power setting of 50 W.



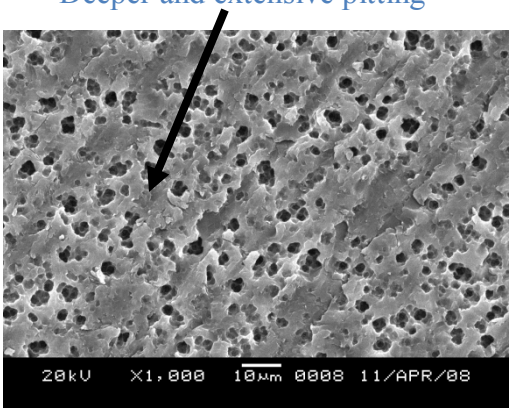
Picture (20) as received Epoxy (high Tg) resin surface (without treatment)

Deeper and more extensive petting



Picture (21) Epoxy (High Tg) surface at 25 W

Deeper and extensive pitting



Picture (22) Epoxy (high Tg) surface at 50 W

4.2.1.1 Discussion of results from the treatment of Epoxy (High Tg) resin

Initially, all results described above obtained under ultrasonic sonication conditions, showed significant changes to the epoxy surface compared to the base value results (Table 4). It is obvious that ultrasonic treatment has a significant impact on the surface of the epoxy sample even at a low power setting (10 W). This fact was observed using all the types of surface analysis methods employed. For example at a power setting of 10 W the sample weight loss was 0.2663 mg/cm^2 and this is much higher than the base value weight loss of 0.0441 mg/cm^2.

However to determine the optimum power setting (ultrasonic intensity) for the surface modification of epoxy samples the combination of results from each diagnostic test has to be taken into account. The highest values for weight loss (Figure 5) and adhesion (Figure 9) were observed at 80 W. The weight loss obtained at this power setting was 0.3186 mg/cm^2 which is almost the same weight loss obtained in the traditional surface modifications using alkaline

permanganate 0.25- 0.45 mg/cm^2 (Goosey and Pool 2004). However for contact angle measurement, the lowest value was observed at 100 W meaning the chemistry of the surface has been changed more at this power setting compared to the other power settings suggesting that an oxidizing species were generated (Cobley and Mason 2008). Changes in the contact angle due to the application of ultrasound were also observed by Price, Keen and Clifton (1996). In their work, a polyethylene (PE) polymer was treated by applying ultrasound with using persulphate as an oxidizing agent. The contact angle of the oxidation outer layer produced via ultrasound showed similar contact angle values to polyethylene samples treated with the conventional chromic acid method.

Where ultrasound treatment using power setting of 100 W has been applied, more water (250 ml) was required to make this power setting work properly. Moreover, the temperature increased quickly compared to lower power settings and at high temperatures the cavitation effects is reduced (Mason and Peters 2002: 9). This reduction is attributed to the bubbles that contain more vapour pressure at high temperature which will be cushioned on collapse leading to less violent collapsing so the cavitational effect is decreased. Roughness (Figure 7) and gloss meter readings (Figure 8) showed very good inverse correlation with each other, with slightly higher roughness occurring with a power setting of 50 W and lower gloss meter value observed at the same power setting. This was expected since gloss should be inversely proportional to the roughness. SEM results indicate that the 25 W and 50 W produced more textured surface which contain extensive pitting. Pictures (21) and (22) showed an etched surface on the epoxy ultrasonically treated samples that have extensive pitting on the surface compared to as received samples. Although adhesion results were all very good (Figure 9), the values were very near to each others. At 80 W a somewhat higher adhesion level was observed. Power setting of 50 W also introduced high adhesion level. At 100 W the adhesion value is slightly lower. So, the optimum power setting for ultrasonic surface modification purpose seems to be between 50 and 80 W as at these inputs, good results are achieved as indicated with most of the analysis methods therefore both powers are used in the following experiments.

4.2.2 Effect of low temperature on the sonochemical surface modification of Epoxy (resin)

It has been mentioned previously that the temperature has an influence on the general cavitation effect when using ultrasound. It has been reported that at a temperature of 35 ºC, cavitation in

water can be enhanced as the production of radicals and attack on the surface of polyethylene has been accelerated at this temperature compared to 55 ºC (Price, Clifton and Keen 1996). It is thought that at lower temperatures than 50 ºC the chemical effect of cavitation, namely radical formation, is increased. Price et al (1996) showed that an increase in the amount of carboxylic groups had been produced at the surface of the examined material (which was polyethylene polymer). However, in more recent work done by Cobley and Mason (2007), Cobley and Mason (2008) a temperature of 40 ºC had been employed as it is more easier to control the sonication process under this temperature (it is more easy to keep the temperature constant than using higher temperature). At higher temperatures the cavitation threshold is lower and less acoustic energy is required to generate cavitation bubbles because the molecular forces within the water become weaker. However, under these conditions the collapse of the cavitation bubbles is also less violent and the general effects of the cavitation are reduced (Mason and Peters 2002: 9). Consequently, lowering the temperature increases violent collapse resulting in more physical effects of the cavitation bubbles. So, using very low temperatures seems to be a promissing concept to obtain a good physical effect from cavitation. The optimum power setting of 80 W and 50 W have been examined at a starting temperature of 0 ºC for all the following experiments. The ultrasonic intensity measurements for these power settings at this low temperature have also indicated that the ultrasonic intensity for these inputs is slightly changed (Table 2).

A- *Weight loss*

In Figure 11 (below), the results for weight loss at low temperature 0 ºC compared to the weight loss at 40 ºC are shown.

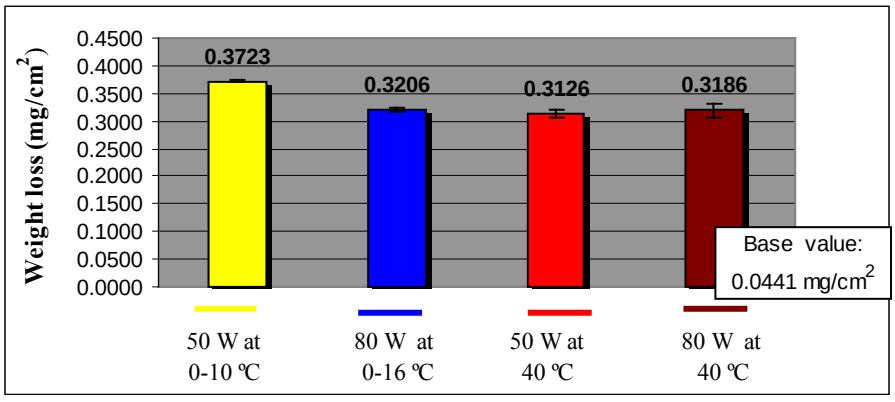


Figure (11) Effect of low temperature on weight loss for Epoxy (high Tg) resin

The results clearly indicate that the greatest material removal at the surface was observed at power setting of 50 W at 0 ºC compared to 50 W at 40 ºC. At 0 ºC where 80 W is used, there is not much difference in weight loss value caused via lowering temperature to 0 ºC compared to a 80 W ultrasound treatment that has been used at 40 ºC.

B- Contact angle

Contact angle measurements at low temperature are shown in Figure 12 and are compared to the measurements observed at 40 ºC for the same power setting. The results are shown as following:

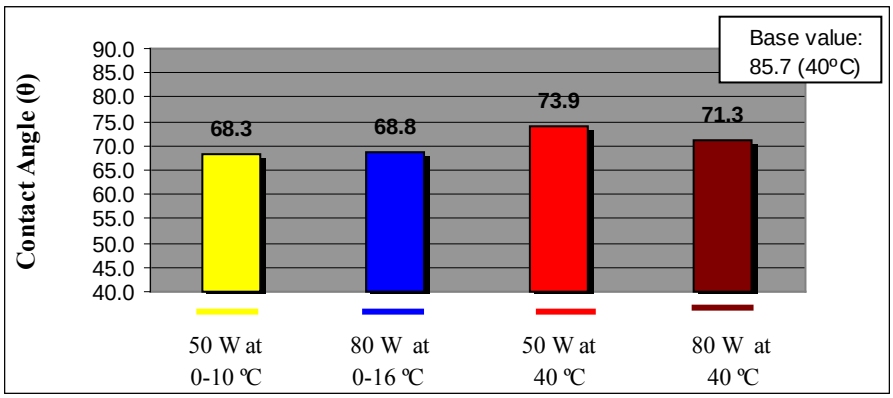


Figure (12) Effect of low temperature on contact angle for Epoxy (high Tg) resin

The results confirm (remembering that lower values for contact angles are preferred) that the chemistry of the surface is mostly changed when 50 W is used at 0 ºC and this was true or almost the same where 80 W is utilized at 0 ºC. These values were lower compared to the same power settings used at 40 ºC.

C- Roughness

In Figure 13, the roughness data obtained at low temperature and compared to the same power setting used at 40 ºC are presented. Results are shown as follows:

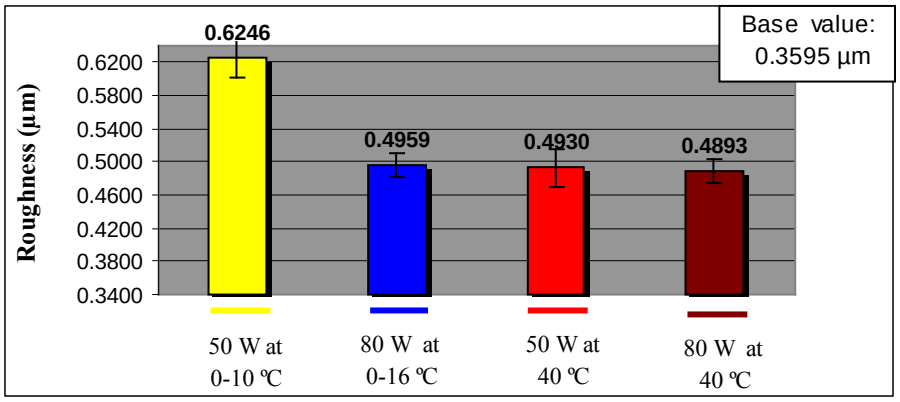


Figure (13) Effect of low temperature on roughness for Epoxy (high Tg) resin

The results obtained in Figure 13 revealed that 50 W at 0 ºC produced the highest roughness readings. The other inputs gave similar results.

D- Gloss meter readings

The gloss meter results for low temperature experiments compared to the ultrasonic treatment using same power settings at 40ºC are shown in Figure 14 as follows:

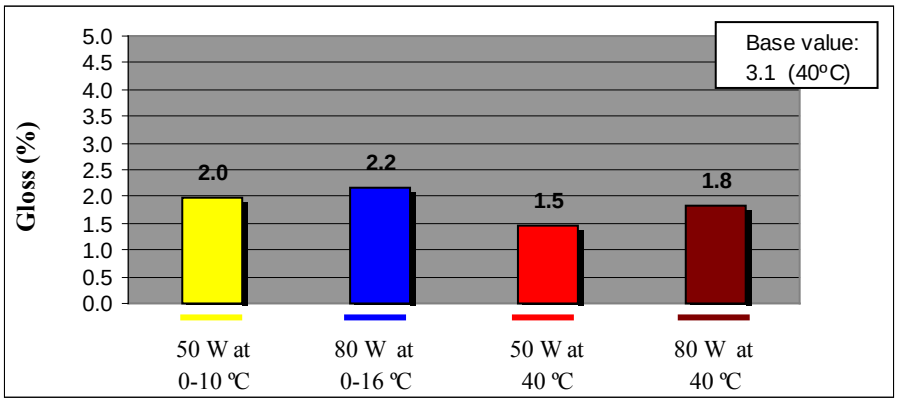


Figure (14) Effect of low temperature on Gloss meter readings for Epoxy (high Tg) resin

A 50 W at 40 ° C produced the lowest gloss meter reading. Generally, the results at high temperature were lower from those obtained for same power setting at 0 ºC remarking that all values were very low. This does not match the roughness reading observed above. However it must be remembered that the gloss meter here all of readings taken from each treatment have values between a narrow ranges of only 2.2 to 1.5 %.

E- Adhesion (Grade)

The adhesion level for low temperature experiments have been assessed visually and compared to the results observed at 40 ºC. the results are shown in Figure 15 as follows:

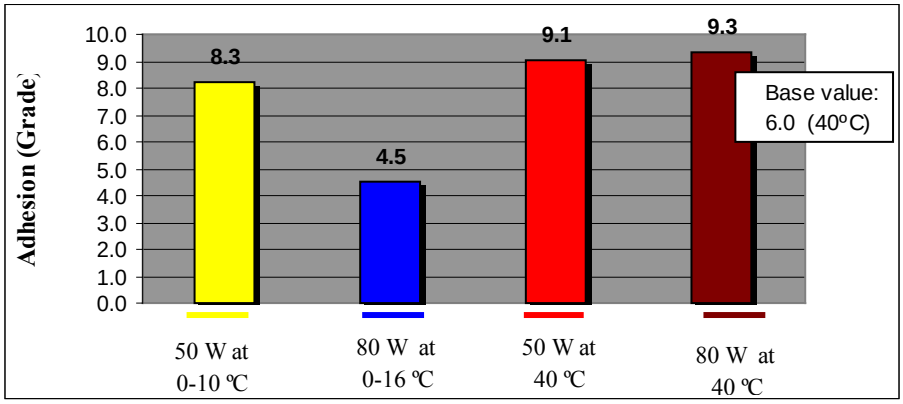


Figure (15) Adhesion grade for Epoxy (high Tg) resin at low temperature

The above data indicates that the adhesion has a good value when employing a power setting of 80 W at 40 ºC which was very close to value obtained for a 50 W at 40 ºC. Lowest adhesion level has been achieved when an 80 W at 0 ºC is utilized.

F- SEM Pictures (Grade)

Pictures were taken via SEM and were graded visually. Grades are presented in Figure 16 as follows:

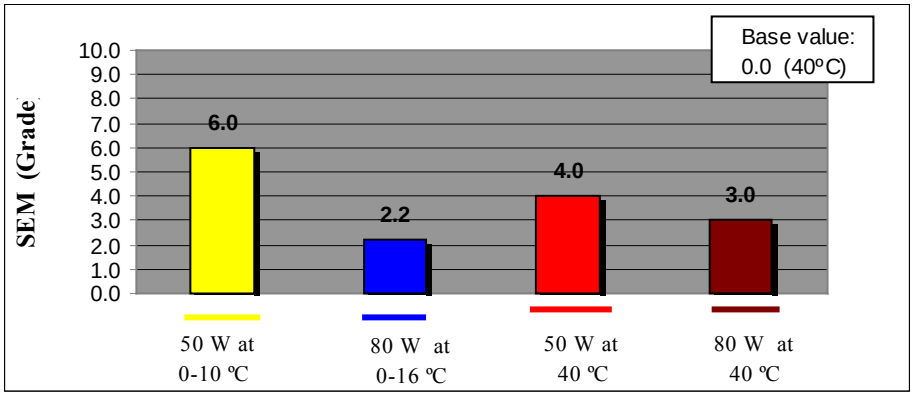


Figure (16) SEM Pictures (Grade) at low temperature for Epoxy (high Tg) resin

These results clearly indicate that lowering the solution temperature caused a significant increase in the texture grade at 50 W where the temperature is 0-10 °C while other conditions have produced lower reading.

4.2.2.1 Discussion

All results obtained above indicate again that ultrasound has a significant influence on the epoxy surface modifications compared to the base line values exhibited in Table 4. However, the weight loss value (0.3723 mg/cm^2) obtained at power setting of 50 W at 0 °C is higher than that obtained when 80 W is used at 40 °C (0.3186 mg/cm^2) . This high value matches again the value obtained using the alkaline permanganate process (Goosey and Poole 2004). Utilizing 50 W at 0 °C caused a decrease in contact angle values referring to a change in the chemistry of epoxy surface and using the same power setting at the same temperature has shown a significant higher roughness value and this fact was confirmed via SEM grade value which is 6 (Figure 16). Gloss meter results did not correlate with the roughness results, possibly due to the similarity in gloss meter readings obtained for all samples.

The effect of lowering the temperature (at 50 W) was expected as it has been confirmed that low temperature can increase the cavitation effects (Mason and Peters 2002: 9). Lowering temperature caused an increasing in the viscosity of water. In addition, the vapour pressure of water is less at low temperature (Mason and Peters 2002: 11). Consequently, the collapse of the cavitational bubbles is more violent when it hits the surface so more material is removed and more roughness surface is obtained. Adhesion results indicate that a higher level of adhesion is produced at 80 W at 40 °C which is almost same as the level at 50 W at 40 °C. Using low temperature produced lower level of adhesion and this could be attributed to the high rough surface for epoxy resin which produced more exposed glass and this could play a factor in lowering the adhesion level due to possible surface debris. This is an additional confirmation that lowering the temperature can enhance the sonochemical surface modification processes. Utilizing a power setting of 80 W at low temperature increases the solution temperature more than 50 W, due to cavitational effects and production of heat via probe vibrations, therefore the overall cavitation effect is reduced.

4.2.3 Effect of frozen samples on the sonochemical surface modification of Epoxy resin

Freezing samples prior to sonication may make the samples more brittle and more amenable to surface modification. When cavitational bubbles are collapsing, these bubbles produce very high

estimated temperatures (4730 °C) and pressures of 2000 atmosphere (Flint and Suslick 1991). Furthermore, this collapse becomes non spherical with high speed liquids moving towards the surface of material and this speed could reach up to 100 m/sec (Plesset and Chapman 1971). Consequently, these cavitation effects are thought to enhance the surface modification if the surface is more brittle at the point of impact.

Epoxy resin samples were placed in the freezer at -2 to 0 ºC for up to 24 hours and then treated via ultrasound at temperatures approximating 0 ºC and 40 ºC. A power setting of 50 W was utilized for all the experiments (see section 3.8). The purpose of this step was to confirm any influence for the temperature on the sonochemical surface modification processes. The results obtained in this section were compared to the results obtained previously under the same conditions (50 W at 40 ºC and 0 ºC) without freezing. Results can be seen as follows:

A- Weight loss

Weight loss results obtained for frozen samples compared to not frozen samples show in Figure 17 as follows:

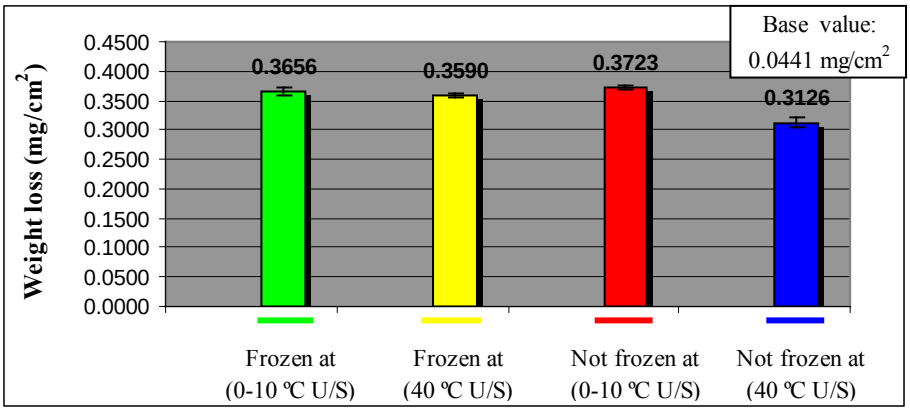


Figure (17) Effect of frozen samples on weight loss for Epoxy (high Tg) resin

Results indicate that the highest material removed was when non frozen sample is treated with ultrasonic power setting of 50 W at 0 ºC. Frozen samples also provided high value but slightly less than to highest value.

B- Contact angle

Results for contact angle measurements for frozen samples are exhibited in Figure 17. These results are compared to the results observed for not frozen samples under the same conditions.

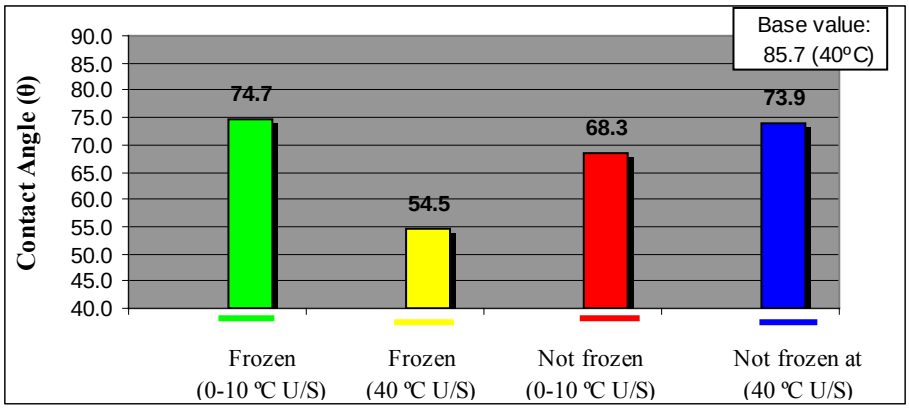


Figure (18) Effect of frozen samples on contact angle for Epoxy (high Tg) resin

The lowest value for contact angle was observed with samples that were frozen and ultrasonically treated at 40 ^{o}C compare to other values obtained at different conditions.

C- Roughness

Roughness results that have been achieved for frozen samples compared to not frozen samples at same conditions are exhibited in Figure 19 as follows:

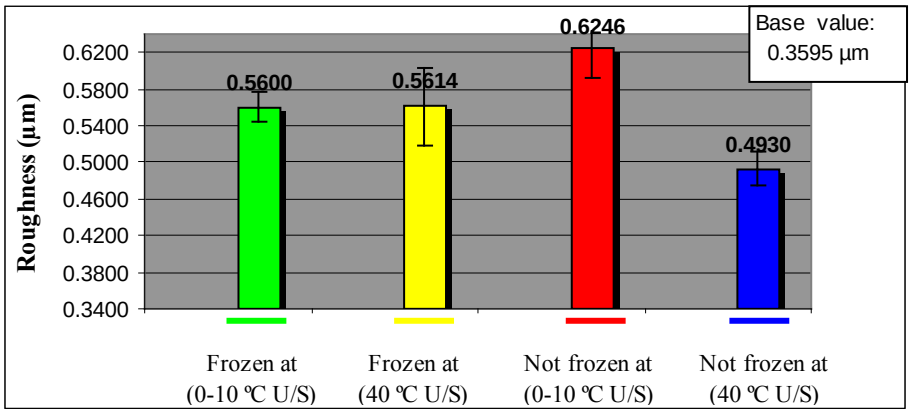


Figure (19) Effect of frozen samples on roughness for Epoxy (high Tg) resin

Although the higher roughness reading was achieved for samples that ultrasonically treated at 0-10 ^{o}C without freezing, frozen samples showed similar degrees of roughness.

D- Gloss meter readings

In Figure 20, gloss meter data obtained for frozen samples compared to not frozen samples are shown as follows:

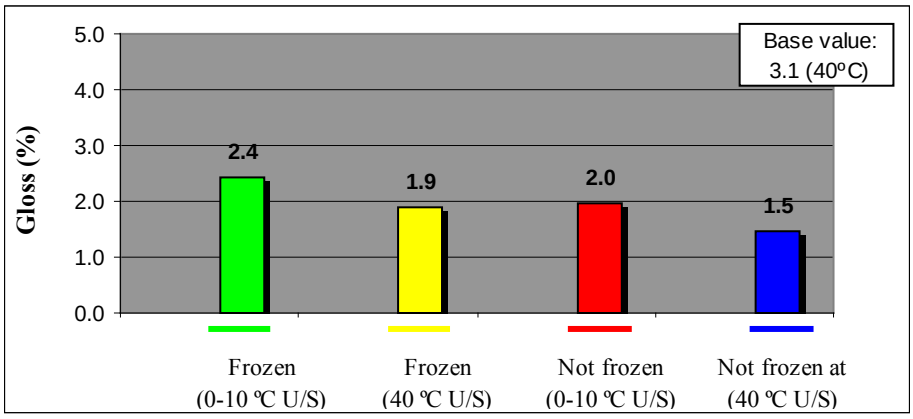


Figure (20) Effect of frozen samples on gloss meter readings for Epoxy (high Tg) resin

The lowest value for gloss meter measurement was achieved when the samples were not frozen and a t emperature of 40 °C was utilized compared to other values obtained at different conditions.

E- Adhesion (Grade)

Adhesion level for the frozen samples has been assessed visually and has been compared to results achieved for the not frozen samples and results are presented in Figure 21 as follows:

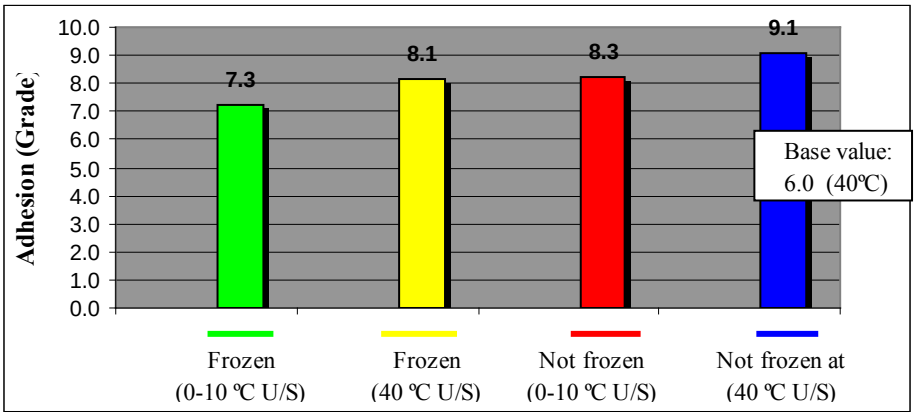


Figure (21) Adhesion grade for Epoxy (high Tg) resin frozen samples

The highest level of adhesion is seen with the non frozen samples at higher temperatures. All adhesion was reasonable.

F- SEM Pictures (Grade)

Scanning electron microscope pictures have been assessed and each picture has been given a grade. Grades are shown in Figure 22 as follows:

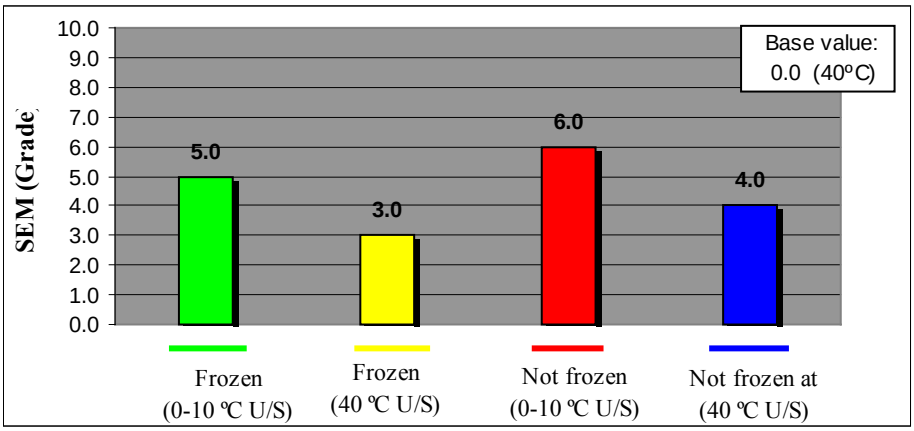


Figure (22) SEM Pictures (Grade) for Epoxy (high Tg) resin frozen samples

Frozen samples produced lower surface texturing compared to the higher value which was obtained with 50 W at 0 ^{o}C.

4.2.3.1 Discussion

It has been previously demonstrated that storing rosemary herbs at 0-4 ^{o}C resulted in increasing in the extraction of some bioactive principles from the rosemary compared to the samples stored at room temperature (Cai 2005). Freezing made the rosemary sample more brittle and more amenable to the desired sonication effects. This suggested that interesting results could be observed with epoxy samples in terms of surface modification processes. The outcome of the experiments with frozen samples revealed that freezing epoxy samples before applying ultrasound did not result in significant effects on the surface modification processes. However, these results are considered as noteworthy compared to the base line values as shown in figures at section 4.2.3. The most important effect for frozen samples was observed in the contact angle value (Figure 18) which has decreased to a value of (54.5 θ) suggesting that the chemistry of the surface has been highly changed for the frozen samples which ultrasonically treated at 40 ^{o}C. On the other hand, contact angle data indicated that a more wettable surface is produced for frozen samples which ultrasonically treated at 40 ^{o}C and this could be considered as an indication for smooth surface formation. The gloss meter results (Figure 20) correlated with contact anglemeasurement in terms of smoothness surface. Overall, results for frozen samples can be considered as a r emarkable in contrast with results obtained by Cobley and Mason (2008) (utilizing 30 minutes and at 40 °C). For instance, the mean weight loss value obtained by Cobley and Mason (2008) was approximately 0.2250 mg/cm^2 while the current value was 0.3590

mg/cm^2. The roughness mean value was 0.5614 µm under current conditions which is higher than the roughness value obtained via Cobley and Mason (2008) which was approximately 0.4000 µm.

4.2.4 Effect of solvents choice on the sonochemical surface modification of Epoxy resin

It has been mentioned in chapter 2 that the choice of solvent has a significant influence on the cavitation formation and the subsequent cavitation effects. Although it is difficult to produce cavitation bubbles within viscous solvents, the temperature and pressure resulting from the collapsing of cavitation bubbles from viscous solvent will be greater than cavitation effects within less viscous solvents (Mason and Peters 2002: 9). Furthermore, the volatile solvents which normally have high vapour pressure will generate cavitation bubbles at low acoustic energy therefore these bubbles will contained more vapour. Vapour filled bubbles whose collapse is cushioned produces less violent collapse compared to the liquids of low vapour pressure (Mason 1999: 11). Indeed, increasing the temperature of the solvents will have the consequence of rising on the vapour pressure of the solvents which lead to decrease the overall influence of the cavitation bubble collapse.

Choosing solvents that have low vapour pressure or have high viscosity could be more desirable for the purpose of surface modification processes for the reasons mentioned above. In addition, these solvents must not be harmful to humans or the environment and it is preferable if these solvents are totally soluble in water (Niemczewski 2005). In addition, the cost of these solvents must be considered. Inexpensive solvents would be more desirable. It has been pointed out in the first chapter that most of the solvents which are utilized in the traditional surface treatment processes, such as sulphuric acid, are very strong and harmful acids. Most electronic industries are considering replacing the traditional solvents for surface modification purpose due to their harmfulness to human health and environment.

NMP (1-Methyl-2-Pyrrolidinone) is one solvent which has been used commonly in traditional surface modification processes for epoxy materials as a “sweller” before alkaline permanganate treatment (Mandich 1994, Thorn and Walsh 1991). This solvent has been employed also for the purpose of increasing the cavitation influence in the ultrasonic cleaning processes due to its full

solubility in water and for its low vapour pressure (Niemczewski 2004). Ethylene glycol is a solvent which has been widely used in Asian countries in the printed circuit board industries (LaDoa,2006) and it is also a widely used solvent to maximise the degree of resin swelling in the Tg resin surface treatment (Goosey and Pool 2004). Butyl carbitol is used as a mixture for swellant step in the alkaline permanganate processes (Mandich 1994). Carano, Polakovic and Lafayette (1999) have disclosed that utilizing a mixture containing butyl carbitol for etch back epoxy residues is a preferred solvent. Finally, Gamma-caprolactone was utilized successfully alone with water or as mixtures with other organic solvents to surface modify Epoxy material (high and low Tg) (Hirst *et al.* 2005). It has been found that Gamma-caprolactone composition could swell the surface of the substrate and after an etchant is applied, a rough surface or a porous resinous substrate is produced. This substrate can provide a mechanical means by which a subsequent deposited metal may anchor onto the substrate and form high strong bond between the substrate and the deposited metal (Hirst *et al.* 2005).

A 5 % (by volume) solution for each solvent was prepared (see 3.9) and the sonochemical processes were applied with an optimum power setting of 50 W and a starting temperature of 0 ºC for all the following experiments. The results obtained for sonochemical experiments were then compared to the base line value for adding solvent without ultrasound treatment (control samples) are shown as follows:

A- Weight loss

Figure 23 shows the results achieved for the effect of adding solvents on the weight loss of epoxy. Results under ultrasonic treatment compared to the base line values are shown as follows:

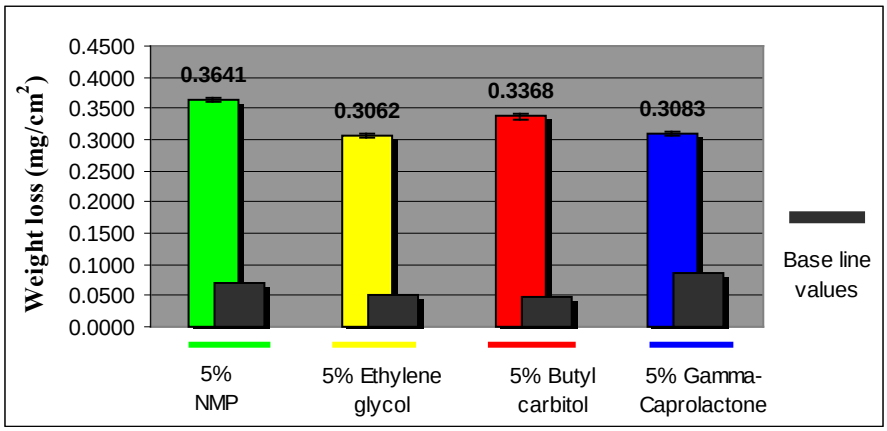


Figure (23) Effect of adding solvents on the weight loss for Epoxy (high Tg) resin

All values are much higher than the base line indicating that ultrasound is having a significant effect. Adding 5 % of NMP (1-Methyl-2-Pyrrolidinone) solvent clearly indicates that a higher amount of material is removed with this solvent. Butyl carbitol produces somewhat less weight loss than NMP, this weight loss value was more than other values obtained by other solvents.

B- Contact angle

Contact angle data which was obtained for the effect of ultrasound on addition of solvents in contrast with base line values is presented as follows:

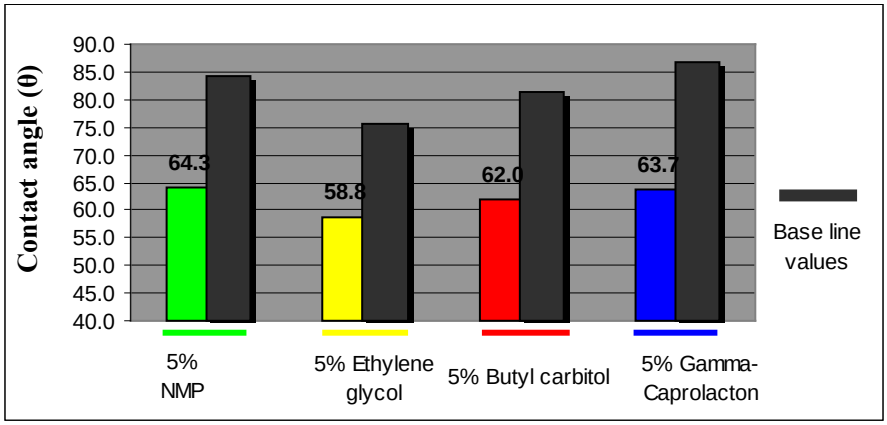


Figure (24) Effect of adding solvents on the contact angle for Epoxy (high Tg) resin

Contact angles values presented in Figure 24 show the effect of adding 5 % (volume) of solvent was almost the same for all the solvents with ethylene glycol producing lower contact angle value compared to other values. All values were lower than base line values after adding solvent which means that ultrasound is having a significant influence.

C- Roughness

Figure 25 s hows the roughness results achieved by using different solvents with ultrasound compared to base line values. Results are shown as follows:

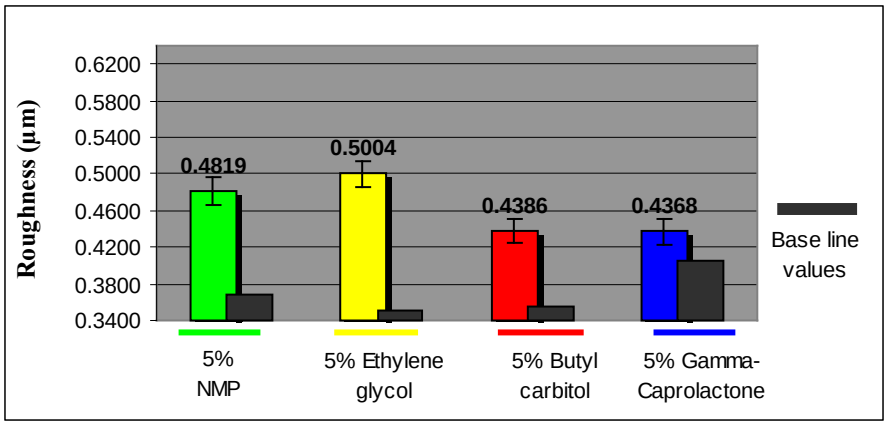


Figure (25) Effect of adding solvents on the roughness for Epoxy (high Tg) resin

A higher roughness value was achieved when a 5 % (by volume) of ethylene glycol was added. NMP also produced high roughness compared to other values. Results were higher than base line values after adding solvent showing that ultrasound had an effect.

D- Gloss meter readings

The influence of adding solvents on the gloss meter % for epoxy material compared to the base line values for same solvents are presented in Figure 26 as follows:

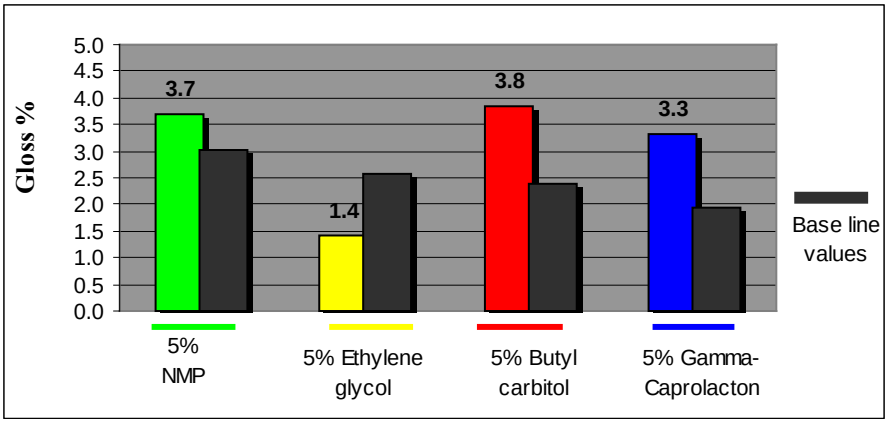


Figure (26) Effect of adding solvents on the gloss meter readings for Epoxy (high Tg) resin

Adding of all the solvents produced higher gloss meter readings in contrast with base line value after adding solvent except ethylene glycol which produced the lower value.

E- Adhesion (Grade)

Adhesion level has been assessed visually for samples treated under additional solvent conditions. Results compared to base line results are shown in Figure 27 as follows:

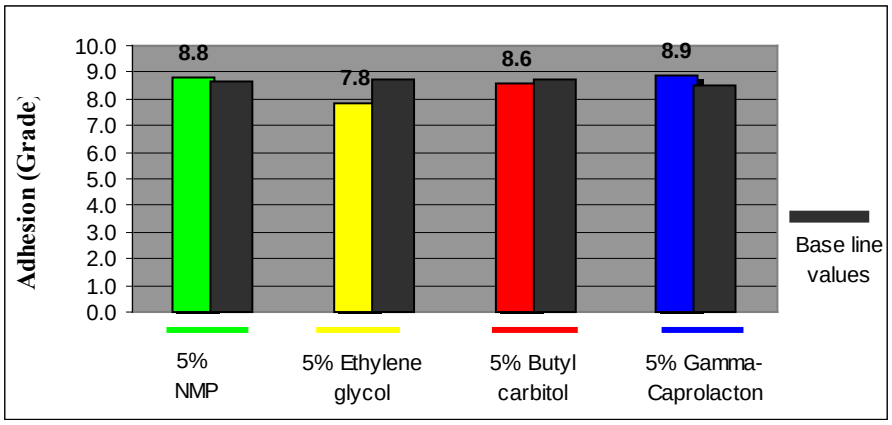


Figure (27) Effect of adding solvents on the Adhesion grade for Epoxy (high Tg) resin

Values illustrated at the above clearly indicate that the treated samples produced almost same values as each other and also the base level results except with ethylene glycol which produced a slightly lower adhesion level.

F- <u>SEM Pictures (Grade)</u>

SEM pictures were graded visually and compared to base line value. Data presented in Figure 28 as follows:

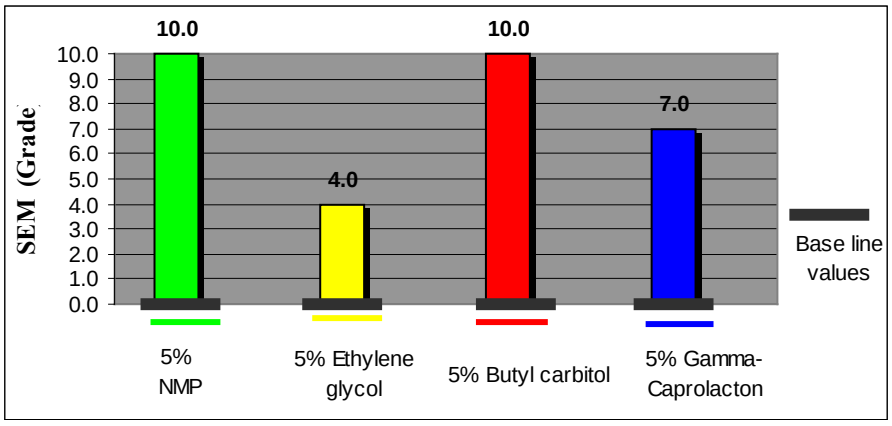
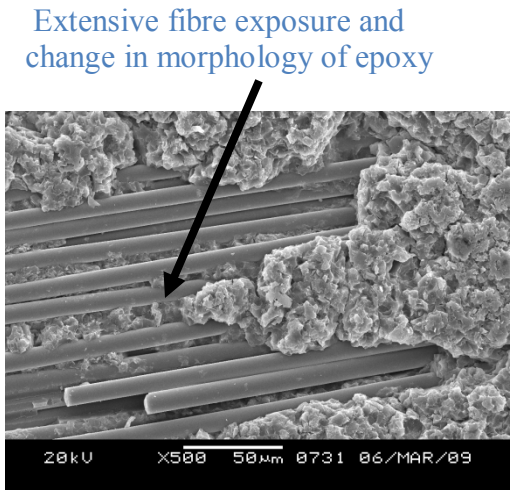


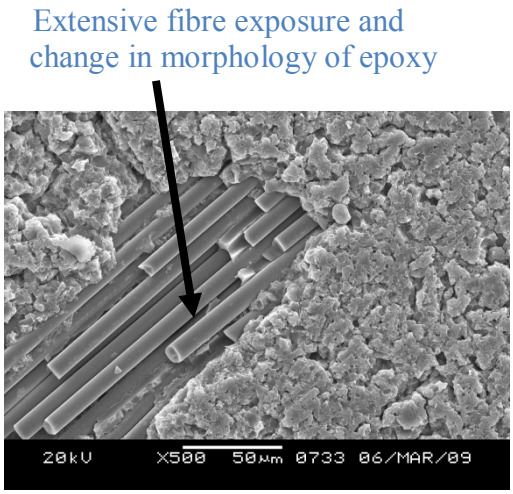
Figure (28) Effect of adding solvents on the SEM Pictures grade for Epoxy (high Tg) resin

Figure 28 indicates that utilizing 5 % NMP and 5 % butyl carbitol solvents have introduced the highest SEM reading (grade 10). Using ethylene glycol or gamma-caprolactone showed lower SEM values. Moreover, Picture (23) shows epoxy surface after ultrasonically treatment with 5 % NMP solvent while Picture (24) presents epoxy surface after ultrasonically treatment with 5 % gamma-caprolactone solvent. Both pictures show a very obvious change in surface appearance

after ultrasonic surface modification. The base line values after adding solvent produced SEM grades which indicated for smooth surface with less or almost no texture surface.



Picture (23) epoxy resin surface with 5 % of NMP at 0-2 °C



Picture (24) epoxy resin surface with 5 % of butyl carbitol at 0-2 °C

4.2.4.1 Discussion

All the results obtained in section 4.2.4 have revealed that utilizing power ultrasound at 20 kHz after added solvents has a significant effect on the surface treatment of epoxy material in contrast with base line values obtained for the solvent experiments. The exemption values were for the gloss meter readings which increased compared to base line values, apart from using ethylene glycol which introduced lower gloss meter reading as it has a very low vapour pressure. NMP and butyl carbitol solvents have shown the more significant effect as the weight loss values for both solvents were the highest (Figure 23) and SEM results have referred to these solvents as the most effective solvent in the term of producing a high textured surface. Picture 23 and 24 has shown an extensive fibre exposure in addition to more changes in the surface morphology. NMP also produced a high degree of roughness on the surface which was slightly higher than butyl carbitol roughness value.

Adding ethylene glycol 5 % (b y volume) produced somewhat varied results which was surprising as this solvent was expected to produce significant results in terms of producing more rough surface as it is widely used for surface modification purpose within the printed circuit

boards companies (Goosey and Pool 2004) for swelling the substrate. This solvent has produced the highest roughness value which was 0.5004 μm (Figure 25) which has been confirmed when the lowest gloss meter readings were achieved with this solvent (Figure 26). Contact angle measurements showed that the lower reading was achieved when 5 % of ethylene glycol was utilized, suggesting that the chemistry of the surface is changing more than base line values particular after using ethylene glycol solvent. In spite of these results, adhesion and SEM results did not correlate with above results as the adhesion reading for ethylene glycol was the lowest among all solvents although there is not big different compared to the adhesion level for other solvents (Figure 27) . The SEM measurements have showed that the lowest grade texture was achieved with ethylene glycol (Figure 28). A slightly lower adhesion achievement for ethylene glycol could be attributed to the high rough surface for epoxy which produced more exposed glass and this could play a factor in lowering the adhesion level due to possible surface debris. In spite of the fact that gamma-caparolactone did not show high values in most of the analysis methods performed, high adhesion level has been obtained with this solvent possibility due to some kind of chemical bond occurring at the surface rather than physical bonding, but this will require further investigation.

The overall outcomes of adding solvents to the ultrasonic treatment, for epoxy (Tg resin), revealed that NMP solvent was the most efficient solvent as a good results of weight loss, roughness, adhesion and SEM grade were obtained. As NMP has been used by other investigators in a mixture of solvents in order to swell epoxy surface (Mandich 1994), this swelling action could be the reason for the ability of this solvent to produce effective results. This effective result is attributed also to the effect of using low temperature during the sonication processes which enhances the cavitation effect and the collapse of the cavitational bubbles is more violent when it hits the surface so more material is removed and more roughness surface is obtained (Mason and Peters 2002: 9).

The aim beyond adding a small concentration of solvents was to enhance the general sonochemical surface modification results which have been achieved on the optimization of power settings experiments. This was done in order to get a close idea about any relevant solvent that can be optimised for further study. Indeed, results acquired in this section can be considered

as a significant in contrast with data obtained by Cobley and Mason (2008) (utilizing 30 minutes and at 40 °C). For instance, the weight loss value obtained via Cobley was approximately 0.2250 mg/cm^2 and roughness reading was approximately 0.4000 µm while the current values were 0.3641 mg/cm^2 which obtained using NMP (5 % by volume) for weight loss and 0.4819 µm for roughness. The weight loss which obtained with all the solvents are almost the same as the reported weight loss achieved via alkaline permanganate processes which is 0.25- 0.45 mg/cm^2 (Goosey and Pool 2004). In spite of all these good results but, adding solvent to surface modify epoxy material did not match those good results which obtained by lowering the sonochemical temperature and using DI water only. For example the higher weight loss obtained for adding solvent was 0.3641 mg/cm^2 while a value of 0.3723 mg/cm^2 was achieved with water only at 0 °C and 50 W. The roughness obtained in this part was (0.4819 µm with NMP) while a value of (0.6246 µm) of roughness was obtained with water only at 0 °C and 50 W

4.2.5 Conclusion

The results from investigation of Epoxy (Tg resin) sonochemical surface modification processes indicates that the optimum power setting for ultrasonic surface modification of this material was between 50 and 80 W as at these inputs, good results were achieved with most of the analysis methods. As a result both power settings have been examined with low temperature experiments. Utilizing Power setting of 50 W at 0-10 °C has shown a noteworthy sonochemical influence rather than utilizing a power setting of 80 W at the same temperature as this power setting increases the temperature of the sonication processes which reduces the cavitation effects. Freezing the material at -2 to 0 °C before applying ultrasound has been tested and showed effective results compared to the base line values. Applying low temperature (0-10 °C) associated with ultrasonic power setting of 50 W presented more significant results than freezing the samples. This fact was observed on adding solvents which also produced good results in contrast with base line values. However, the most significant results were achieved when a power setting of 50 W at 0-10 °C was utilized because at this condition, the highest values for weight loss and roughness have been obtained in addition to high level of adhesion. It must be taken into the account that using solvents particularly NMP solvent produced a high level of surface texture which also produced good adhesion level.

4.3 ABS SONOCHEMICAL SURFACE MODIFICATION

Acrylonitrile-Butadiene-Styrene (ABS) is an important engineering plastic which is widely used in the metal finishing and automotive manufacturing industries due to its highly thermal stability, excellent mechanical strength and high resistance to chemical reagents (Tang *et al.* 2009). It is still commonly utilized in phone and mobile casings and their entire components. ABS plastic is a polymer which consists of three monomers acrylonitrile, butadiene and styrene. It is a robust plastic with good chemical resistance to both mineral acids and alkalis (Groshart 1972). Traditional surface modification utilizing chromic acid (CrO_3) is one of the oldest and the most commonly employed methods to surface modify ABS plastic (Ghorashi 1977). Using chromic acid nowadays is becoming problematic, particularly as chromic acid generates hexavalent chromium residues (Cr^{6+}) which are very toxic and introduce serious operational problems such as contaminating the subsequent electroless plating process (De Bruyn *et al.* 2003). ABS plastic was reported to be suitable to be surface modified via power ultrasound (Cobley and Mason 2008). In this project a few parameters (low temperature, frozen samples and the effect of adding solvents) have been examined to consider achieving these ultrasonic effects.

Several coupons of ABS have been analysed via several methods in order to establish a base line value which ultrasonic results could compared to. All the coupons were immersed in DI water for 15 minutes at 40 ºC and then all the analysis methods the surface of the ABS samples were utilized. The results are the average values of three repeat tests which tabulated as follows:

Weight loss (mg/cm^2)	Contact angle (θ)	Roughness (µm)	Gloss Meter %	Adhesion (Grade)	SEM (texture) (Grade)
-0.0176	**85.7**	**0.0554**	**86.2**	**0.0**	**0.0**

Table 5, Base line value results for ABS

Unusually as can be seen in the above Table (5) there was no weight loss value observed for ABS after treatment in water. Instead a small weight gain is observed. This could be attributed to the absorption of water by ABS and for this reason the material could gain some weight after being immersed in DI water.

4.3.1 The optimization of power setting for sonochemical surface modification using ABS material.

Experiments were carried out to determine the optimum power settings for the ultrasonic probe which could be useful in the following experiments. The results obtained are exhibited as follows:

A- Weight loss

Results for weight loss at different power settings for ABS are exhibited in Figure (29) as follows:

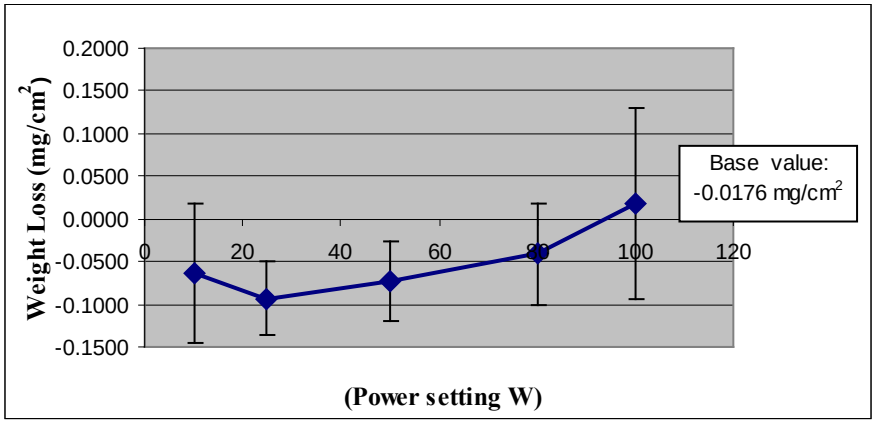


Figure (29) Weight loss for ABS at different power settings

There is a clear indication from Figure 29 that there is no weight loss for ABS except at power setting of 100 W which produced a very small weight loss value. This was highly unexpected. However it should also be noted that all values were very small compared to base line values probably indicating that virtually no effect had occurred on the material.

B- Contact angle

Figure 30 presents the contact angle measurements obtained for ABS at different power settings. Data are shown as follows:

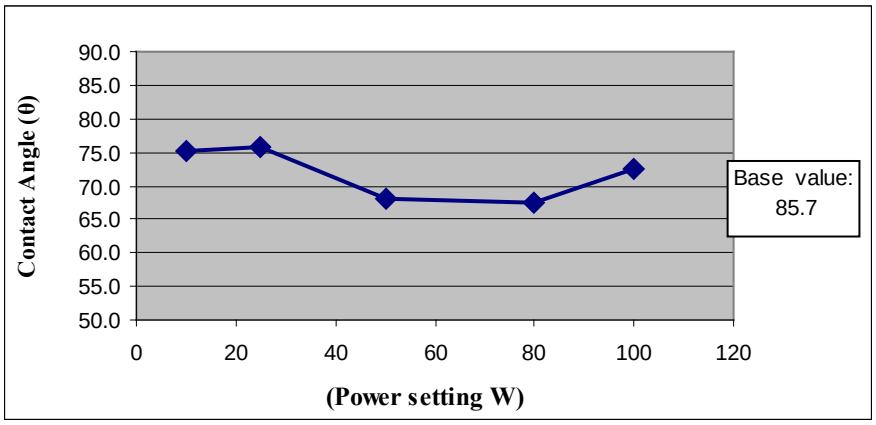


Figure (30) Contact angle for ABS at different power settings

Data in figure 30 shows a drop in the contact angle values particularly at 5a power settings of 50 W and 80 W. The value increased at the power setting of 100 W.

C- Roughness

Values achieved for ABS roughness measurement are presented in Figure 31 as follows:

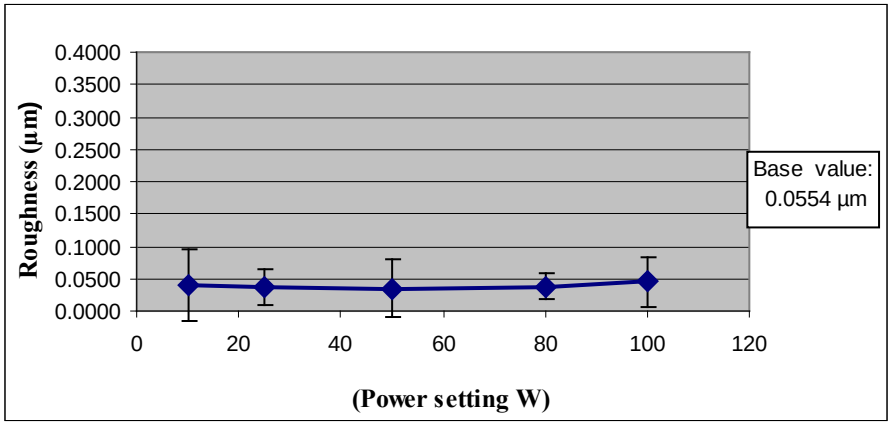


Figure (31) Roughness for ABS at different power settings

Results indicate that almost no difference roughness values obtained at different power settings indicating that a very slightly higher value for roughness was obtained at a power setting of 100 W and 25 W.

D- Gloss meter readings

Gloss meter values were obtained at different power settings for ABS are presented in Figure 32 as follows:

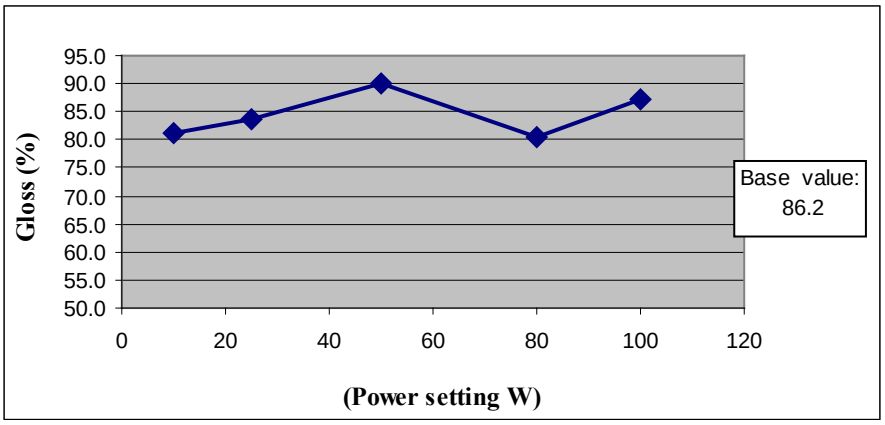


Figure (32) Gloss meter readings for ABS at different power settings

The lowest value for gloss meter readings was seen at power setting of 50 and 80 W. A peak was observed at 50 W and 100 W.

E- Adhesion (Grade)

Adhesion levels have been determined visually for different power setting. Levels grade obtained are shown as follows:

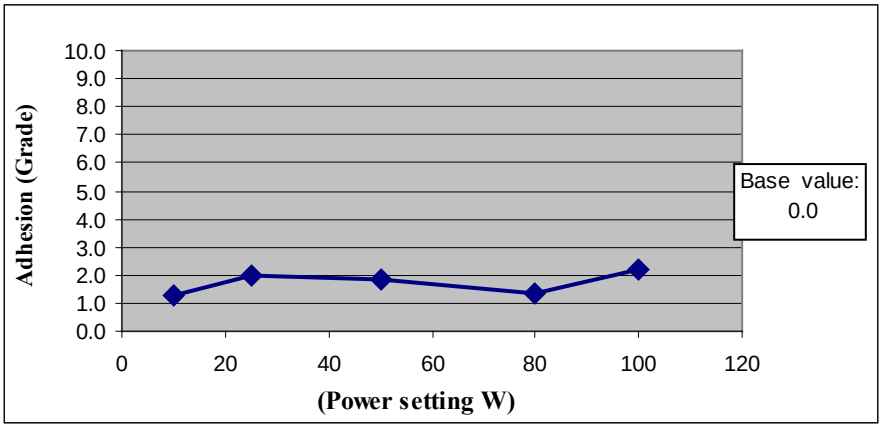


Figure (33) Adhesion grade for ABS at different power settings

A slight higher rate of adhesion was observed at a power setting of 100 W. However, a power setting of 25 and 50 W also provided a higher level of adhesion compared to other adhesion values. However it should be noted that all values are very low and would be considered as unacceptable.

F- SEM Pictures (Grade)

SEM pictures for different power setting have been assessed and each picture has been given a grade. The results are shown in Figure 34 below.

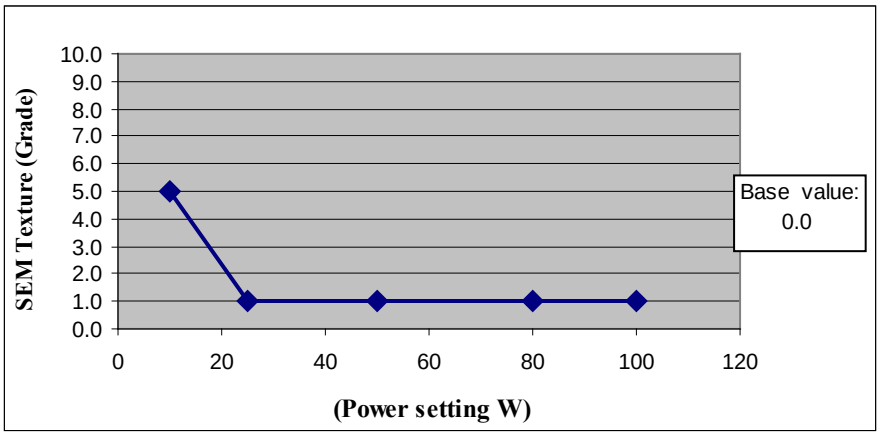
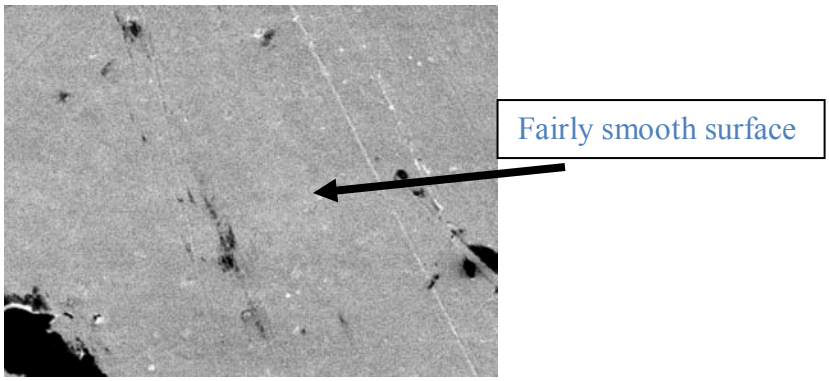
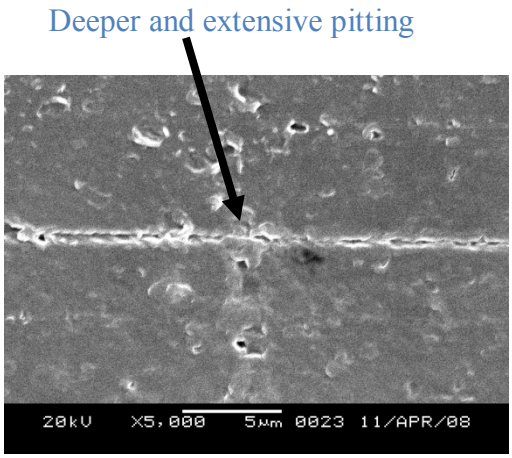


Figure (34) SEM Pictures (Grade) for ABS at different power settings

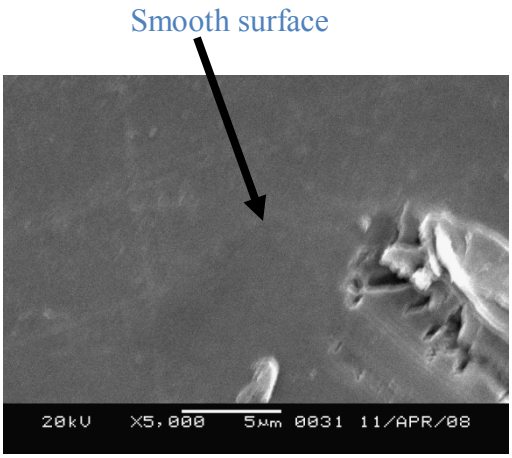
Results indicate that higher texture grade was produced when a power setting of 10 W is used compared to other results. Other power settings give the same texture grade which is low. Furthermore, Picture (26) shows a surface that has few pits or microcavities while Picture (27) shows a surface which almost was the same for as received samples (without any microcavities).



Picture (25) ABS as received



Picture (26) ABS surface at 10 W



Picture (27) ABS surface at 80 W

4.3.1.1 Discussion

The weight loss results for ABS material obtained by applying ultrasound were negative perhaps indirectly suggesting that a slight swelling has been produced at the surface. This very slight gain on the weight has matched the results by Cobley and Mason (2007). The only weight loss achieved was when a power setting of 100 W was applied and this value was not noteworthy. ABS might absorb water and find it very difficult to lose it. Changing the surface of ABS from a hydrophobic nature by using chromic acid to a hydrophilic nature has been confirmed via Mandich and Krulik (1993). This could be considered as an evidence Mandich and Krulik (1993) about the ability of ABS to absorb water particularly if some type of oxidizing reaction occurred at the surface possibly by the free radicals generated via ultrasound. Traditional methods using chromic acid have demonstrated that a polar group such as carboxylic group has been formed on the ABS surface via oxidizing the surface and these groups are the reason for making the surface more hydrophilic (Mandich and Krulik 1993).

Roughness (Figure 31) measurements produced values which were very slightly less than the base line value (0.0554 μm) which means that no significant effect on roughness was observed. Cobley and Mason (2007) produced similar results with ABS using 60 minutes sonication at 40 °C. Contact angle results (Figure 30) signify that ultrasound could change the chemistry of the ABS surface. The contact angle value decreased at 50 W and 80 W sequentially and the roughness results at this particular power settings correlate with contact angle measurement suggesting a smooth surface is produced. Gloss meter measurements did not correlate with other results obtained with other power settings except at power setting of 100 W which suggests that a slight rough surface is produced. Reference to Figure 34 which shows that the surface of ABS is very smooth except at power setting of 10 W as SEM Picture 26 showed somewhat higher texture grade as it contained extensive and deeper pitting on the surface. It must be pointed out that this effect was localized and does not represent the whole surface while ABS surface after traditionally treated via chromic acid shows microcavities distributed over the whole surface (Poa, Wan and Wu 1977). Although adhesion results were generally very poor, higher adhesion was obtained at a power setting of 100 W which correlates with weight loss, roughness and gloss meter results.

The most convenient or optimal power setting for ultrasonically treating ABS samples was 100 W where weight loss, higher roughness value and higher adhesion level are obtained at this power setting but, as it has been mentioned previously that at a power setting of 100 W more amount of water (for sonication) is required and the temperature of the process increases very rapidly and the general effects of the cavitation are reduced (Mason and Peters 2002: 9). Therefore more water is needed to cool down the ultrasonically surface treatment processes. Furthermore, the efficiency of the probe is reduced as after 5-6 minutes from starting of the process a power setting approximately 85 W is reached which is near the power setting of 80 W. Consequently, using 80 W seems to be more convenient as the temperature can be controlled more easily and it would be better to utilize less amount of water to cool down the system particularly from an economic and environmental point of view. So the power setting of 50 W and 80 W was utilized in the following experiments in the section 4.3.2 as temperature control is easier with these two power settings

4.3.2 Effect of low temperature on the sonochemical surface modification of ABS

The chosen power setting of 80 W and 50 W has been examined at a starting temperature of 0 ºC for all the following experiments. The results obtained are compared to the results at same power setting achieved in previous experiments which have been performed at 40 ºC. The results are exhibited as follows:

A- Weight loss

The results for weight loss at low temperature compared to the weight loss at 40 ºC for same power settings are shown as follows:

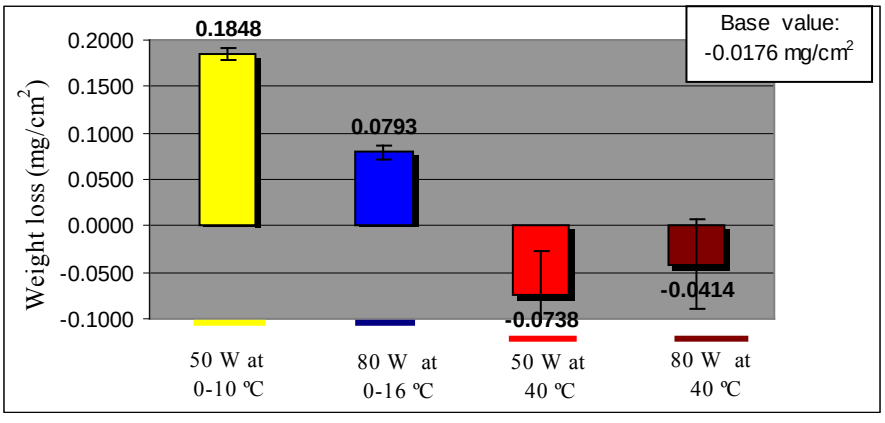


Figure (35) Effect of low temperature on weight loss for ABS

Utilizing 50 W at 0 °C produced the higher weight loss value for ABS material. Lowering temperature at 80 W also produced weight loss but less than 50 W. power settings at 40 °C produced a weight gain.

B- Contact angle

Contact angle values at low temperature are shown in Figure 36 and were compared to the values observed at 40 ºC for the same power setting. The results were as follows:

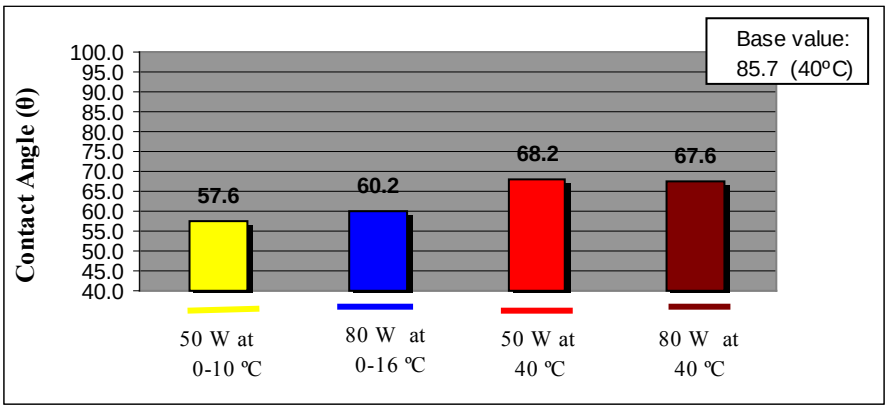


Figure (36) Effect of low temperature on contact angle for ABS

Figure 36 clearly indicates that a lower contact angle value was produced at 50 W power ultrasound setting when a t emperature of 0 ºC is used. Power setting of 80 W at 0 ºC also produces a low value but slightly higher than 50 W.

C- Roughness

The roughness data obtained at low temperature and compared to same power setting used at 40 ºC are presented in Figure 37 as follows:

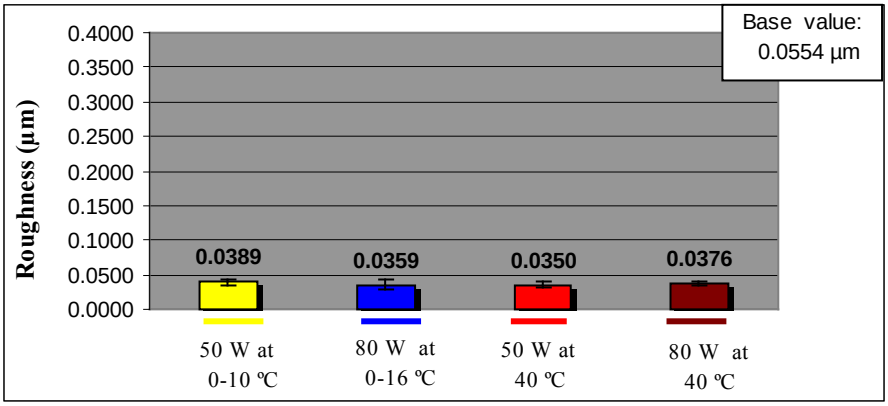


Figure (37) Effect of low temperature on roughness for ABS

Roughness measurements show very close values, indicating that no significant results were obtained compared to roughness base value which was 0.0554 µm.

D- Gloss meter readings

Gloss meter results for low temperature experiments compared to same power setting achieved at 40 ºC are shown in Figure 38 as following:

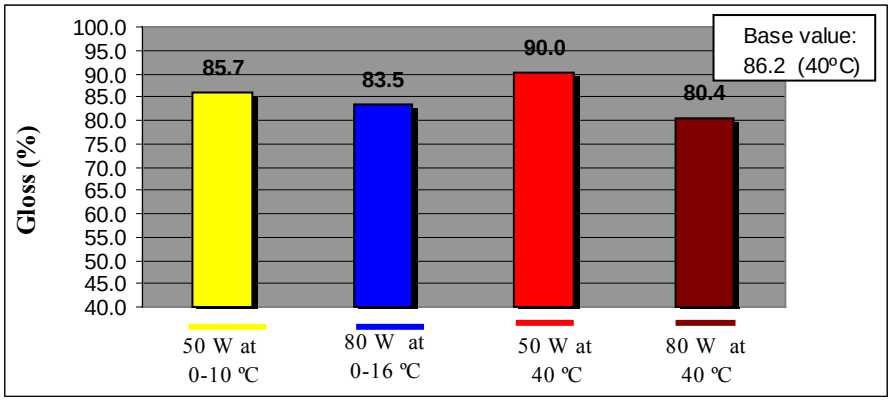


Figure (38) Effect of low temperature on Gloss meter readings for ABS

The data shown in the above figure indicates that using the ultrasonic probe at a setting of 80 W at 40 ºC were the conditions which produced the lowest value for gloss meter readings.

E- Adhesion (Grade)

Adhesion level for low temperature experiments have been assessed visually and compared to the results observed at 40 ºC for same power settings. The results are shown in Figure 39 as follows:

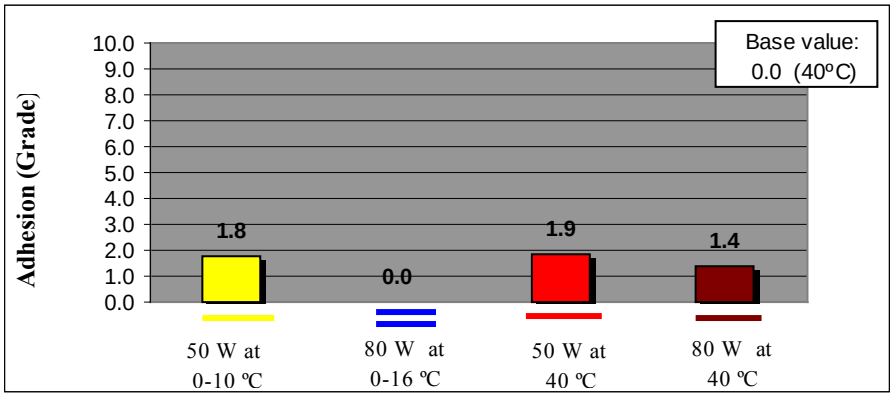


Figure (39) Adhesion grade for ABS at low temperature

All the adhesion levels were very poor remarking that a slight high adhesion level was produced at 50 W at 0-10 ºC and 40 ºC the temperature utilized compared to 80 W.

F- SEM Pictures (Grade)

Pictures were taken via SEM and were graded visually. Grades are presented in Figure 40 as following:

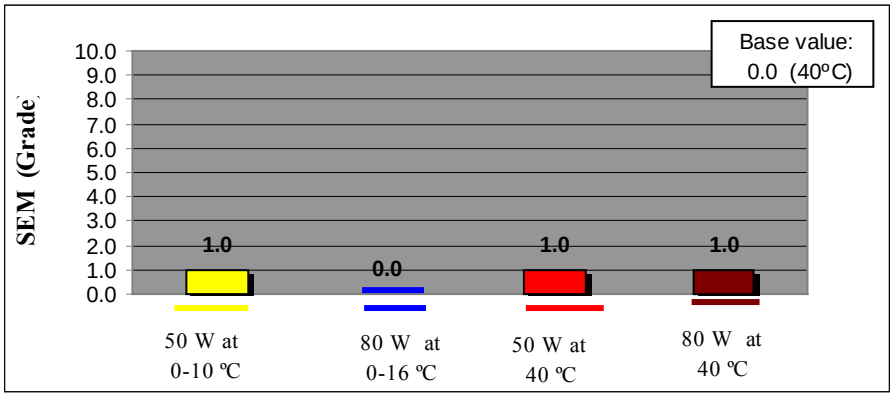


Figure (40) SEM Pictures (Grade) for ABS at low temperature

SEN results indicate that lowering the temperature does not have a significant influence on surface morphology when using ultrasound at different conditions. All values were the same (very poor outcomes) except when an 80 W is utilized at 40 ºC and produced a surface which was graded as 0 surface morphology which means that surface was very smooth as for the received samples.

4.3.2.1 Discussion

Generally, the results for ABS material obtained in the low temperature experiments showed that lowering the temperature has a significant influence on some of the factors increasing the ultrasonic treatment for this material. Weight loss values (Figure 35) have been increased via lowering the temperature. The removal of this amount of the material (1848 mg/cm^2) could not be achieved at 40 °C, and it is much higher than the weight loss obtained for the same material in work performed at 40 °C for 30 minutes by Cobley and Mason (2008) which was approximately 0.1500 mg/cm^2. Roughness values were almost the same for all the samples obtained at different conditions. The contact angle results (Figure 36) showed a dropping in the contact angle values by employing low temperature and these results correlate with gloss meter measurements. Both

results indicated that a smooth surface for ABS material is produced at low temperature. Although the microjetting effect for cavitation increases at low temperature (Mason and Peter 2002: 13), the surface of this material is very glossy and the cavitation effect seems to occur via removing some amount of materials from the surface. Meanwhile as the cavitation cleans the surface a hydrophilic and smooth surface is produced. ABS hydrophilic surface was claimed to be achieved (determined using X-Ray photoelectron spectroscopy) by using chromic acid and this produces a chemical bond between the substrate and the subsequent metal (Mandich and Krulik 1993). Adhesion results (Figure 39) and SEM grades (Figure 40) indicate that low temperature does not enhance the ultrasonic effect in terms of improving the adhesion or the surface texture on the ABS surface. Moreover, utilizing a power setting of 80 W at low temperature did not produce any level of adhesion and texture on the surface.

4.3.3 Effect of frozen samples on the sonochemical surface modification of ABS

ABS samples were placed in the freezer at -2 to 0 ºC for up to 24 hours and then treated via ultrasound at temperatures approximating 0 ºC and 40 °C. A power setting of 50 W was utilized for all the experiments (see section 3.8). The results achieved in this part were compared to those obtained previously at the same conditions (50 W at 40 °C and 0 °C) without freezing. Results were as follows:

A- Weight loss

Weight loss values achieved for frozen samples compared to not frozen samples at the same conditions are shown in Figure 41 as follows:

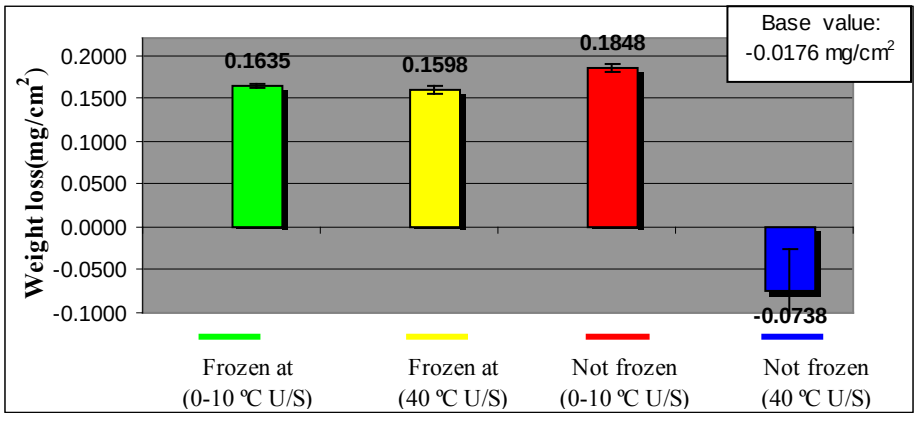


Figure (41) Effect of frozen samples on weight loss for ABS

Figure 41 indicates that the value of weight loss values for the frozen samples at both temperatures was higher than the values for not frozen samples treated at 40°C. Utilizing 0 °C with non frozen samples produced a slight higher weight loss value.

B- Contact angle

In Figure 42, results for contact angle measurements for frozen samples are exhibited and compared to not frozen samples under the same conditions.

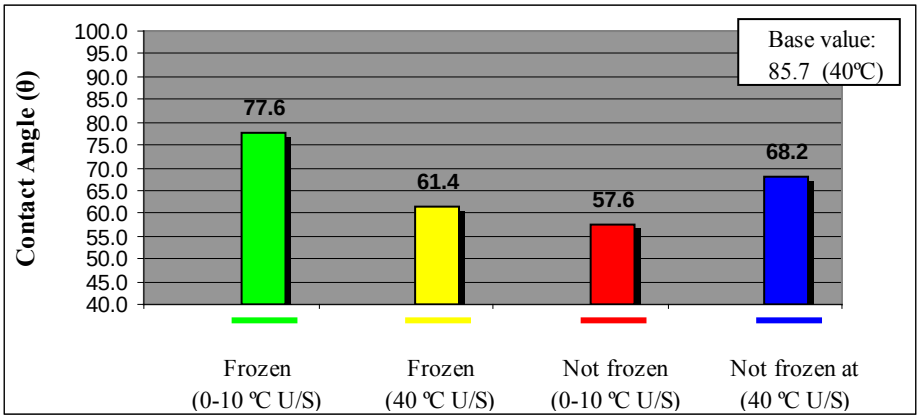


Figure (42) Effect of frozen samples on contact angle measurements for ABS

A lower contact angle value is observed for non frozen samples sonicated at 0-10 °C. Frozen samples treated with ultrasound at 40 °C showed also lower values compared to not frozen samples at the same temperature.

C- Roughness

Roughness results achieved for frozen samples compared to not frozen samples at same conditions are presented in Figure 43 as follows:

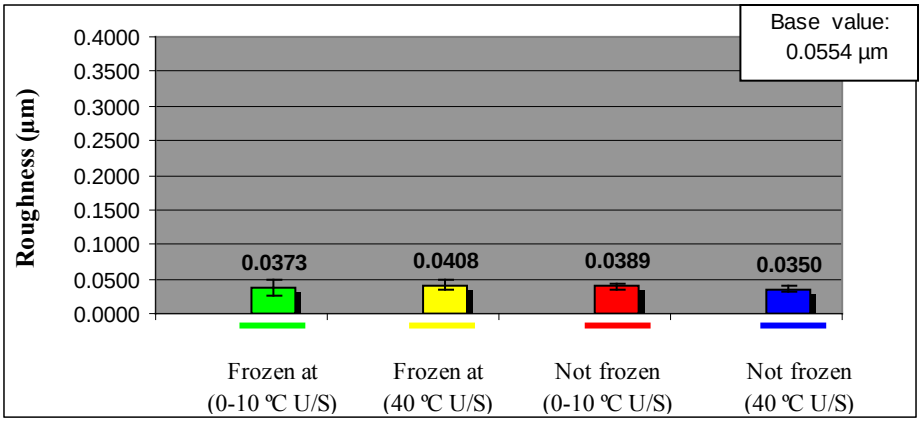


Figure (43) Effect of frozen samples on roughness for ABS

Values achieved at different conditions were very close. Frozen samples (40 °C) showed that roughness value was slightly higher than all the other reaction conditions.

D- Gloss meter readings

Gloss meter values for frozen samples are compared to not frozen samples under the same reaction conditions are shown as follows:

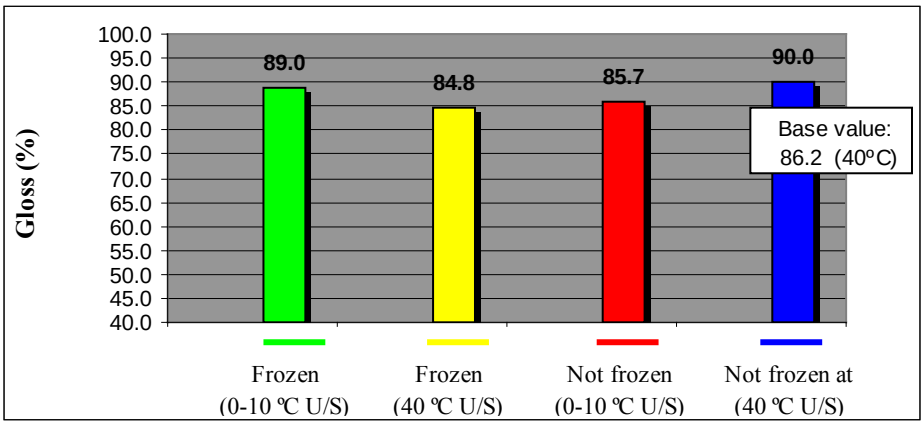


Figure (44) Effect of frozen samples on gloss meter readings for ABS

Gloss meter values indicate the lowest data is observed for frozen samples at 40 °C which was slightly higher than the value obtained for not frozen samples at 0-10 °C.

E- Adhesion (Grade)

Adhesion levels for the frozen samples have been assessed visually and were compared to results achieved for not frozen samples under the same conditions. Results are presented as follows:

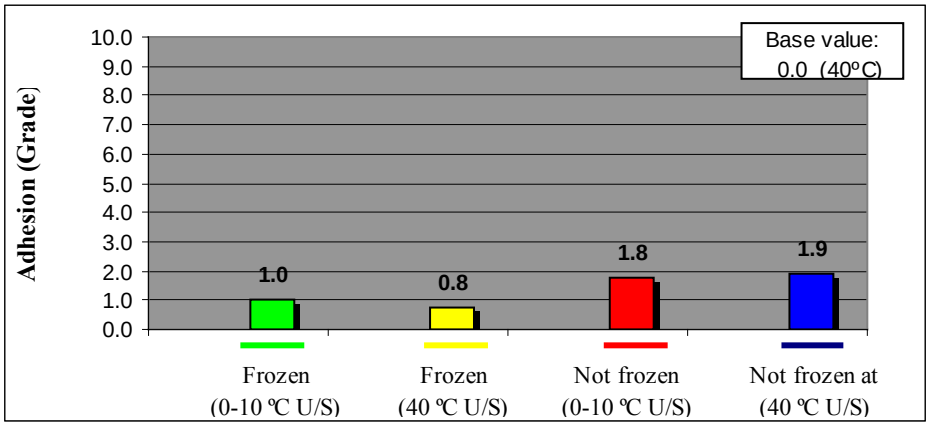


Figure (45) Adhesion level (Grade) for ABS frozen samples

All adhesion results were very poor. Not frozen samples showed higher adhesion reading than frozen plaques.

F- SEM Pictures (Grade)

SEM pictures have been assessed and each picture has been graded as follows:

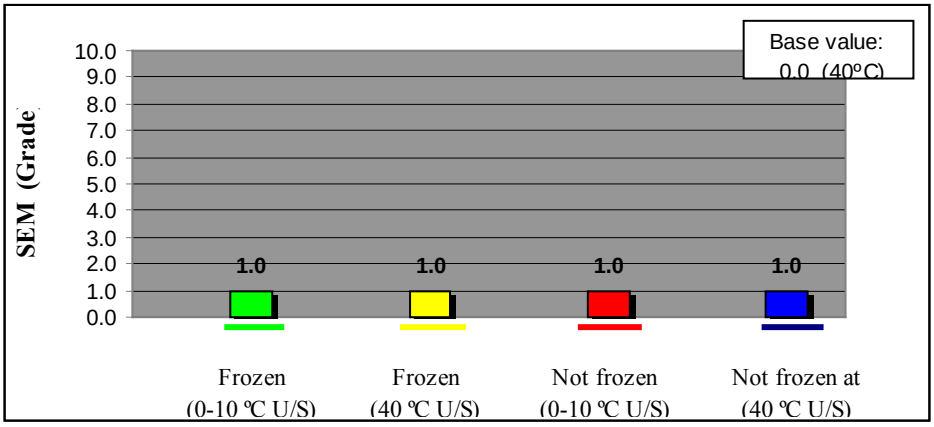


Figure (46) SEM Pictures (Grade) for ABS frozen samples

Results shown in Figure 46 indicate that the surface morphology of pictures for non frozen samples produced after treatment was same for all conditions.

4.3.3.1 Discussion

Taking into account all the results obtained for frozen sample experiments, freezing ABS samples before treatment produced significant results compared to base line values as it is shown on the above figures. These results could also be considered as being significant in contrast with results obtained by Cobley and Mason (2008) which were achieved by utilizing 30 minutes of ultrasonic treatment at 40 °C while our results for frozen samples were obtained utilizing 15 minutes at 40 °C. Weight loss value obtained by Cobley and Mason was approximately 0.0200 mg/cm^2 and roughness was approximately 0.0200 µm while with frozen samples the values were 0.1598 mg/cm^2 for weight loss and 0.0408 µm for roughness value.

Weight loss (Figure 41) and contact angle (Figure 42) results indicate that lowering temperature only, without freezing, produced desirable results when a low temperature is used. Roughness data indicates that frozen samples treated at 40 °C produced slightly higher value in contrast with

value obtained for not frozen samples at 0-10 °C while gloss meter results do not correlate with roughness results and indicates that the smoothness surface could be produced with frozen samples at 40 °C. Figure 45 showed that poor level of adhesion is achieved via freezing the samples. SEM grades showed that the surface morphology for all the samples was poor at all conditions. It is possible that the microjetting effect occurred at the surface (Cobley and Mason 2008) and was able to remove material from the ABS surface and cleaning the surface without seeming to produce any microcavities on the surface which are produced when chromic acid is utilized due to the dissolution of butadiene.

4.3.4 Effect of adding solvents on the sonochemical surface modification of ABS

ABS samples have been sonochemical surface modified with four solvent solutions. A 5 % (volume) solution for each solvent has been prepared (see 3.9) and the sonochemical processes applied with optimum power setting of 50 W that have been used at a starting temperature of 0 ºC for all the following experiments. The results obtained for sonochemical experiments compared to the base line value for adding solvent (control samples) are shown as follows:

A- Weight loss

Figure 47 shows results obtained for the effect of adding solvents on the weight loss of ABS. Results under ultrasonic treatment compared to the base line values are shown as follows:

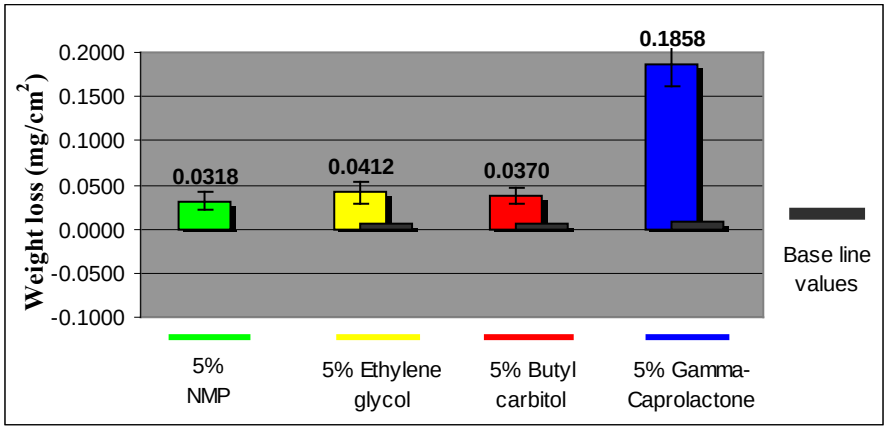


Figure (47) Effect of adding solvents on the weight loss for ABS

There is a clear indication from Figure 47 that the higher weight loss for ABS was achieved when a 5% (by volume) of gamma-caprolactone solvent was used for ultrasonic treatment.

Weight loss results for other samples were slightly similar with remarking that these values were higher than results for base line values meaning that adding solvent with ultrasound have a significant effect.

B- Contact angle

Contact angle readings which were obtained for the effect of ultrasound for different solvents compared to base line values are illustrated as follows:

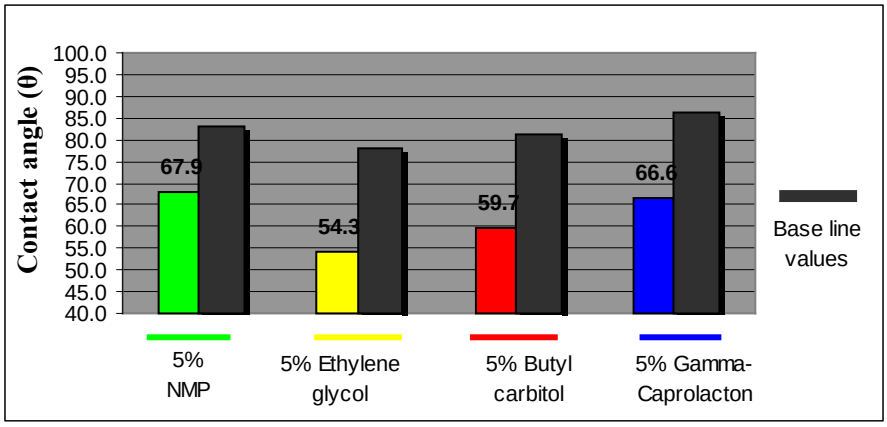


Figure (48) Effect of adding solvents on the contact angle for ABS

All the values obtained for contact angle were lower than base line values showing a significant influence of adding solvent in combination with ultrasound. The lower value for contact angle is observed for samples that were treated ultrasonically with 5% ethylene glycol solvent. 5% butyl carbitol also produced somewhat similar value.

C- Roughness

Roughness results achieved by using different solvents with ultrasound compared to base line values for ABS are shown in bottom as follows:

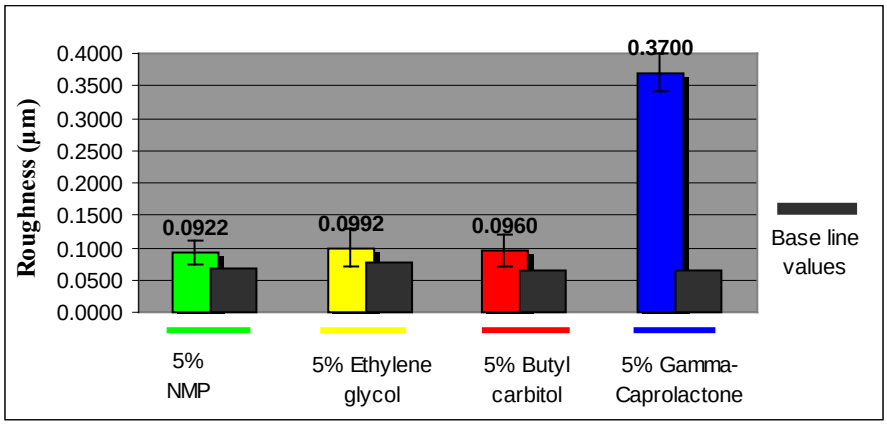


Figure (49) Effect of adding solvents on the roughness for ABS

All the results achieved were higher than base line results showing again the big effect for ultrasound with adding solvents. A higher roughness value is produced when a 5 % of gamma-caprolactone is added compared to other solvents result.

D- Gloss meter readings

The influence ultrasound with use various solvents on the gloss meter % for ABS material compared to the base line values for same solvents are presented in Figure 50 as follows:

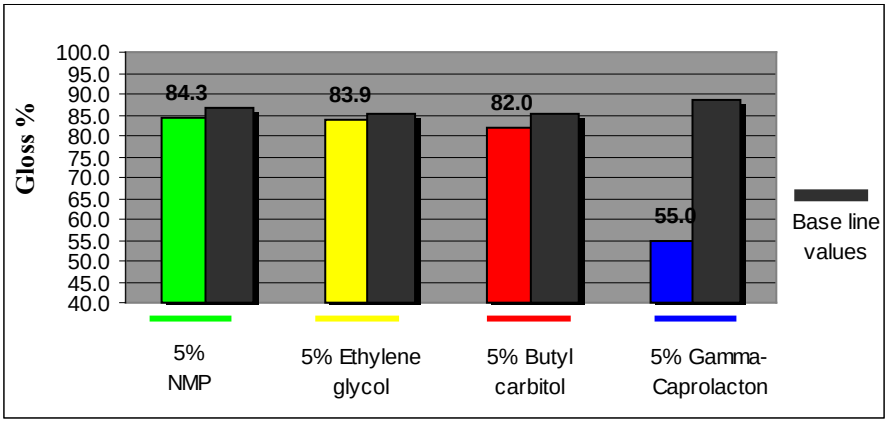


Figure (50) Effect of adding solvents on the gloss meter readings for ABS

It is obvious that utilizing NMP, ethylene glycol and butyl carbitol gave a slight similar gloss meter reading. Gamma-caprolactone was the solvent which produced the lower gloss meter reading.

E- Adhesion (Grade)

Adhesion level has been assessed visually for ABS samples treated via ultrasound with additional solvent conditions. Results compared to base line values are shown in Figure 51 as follows:

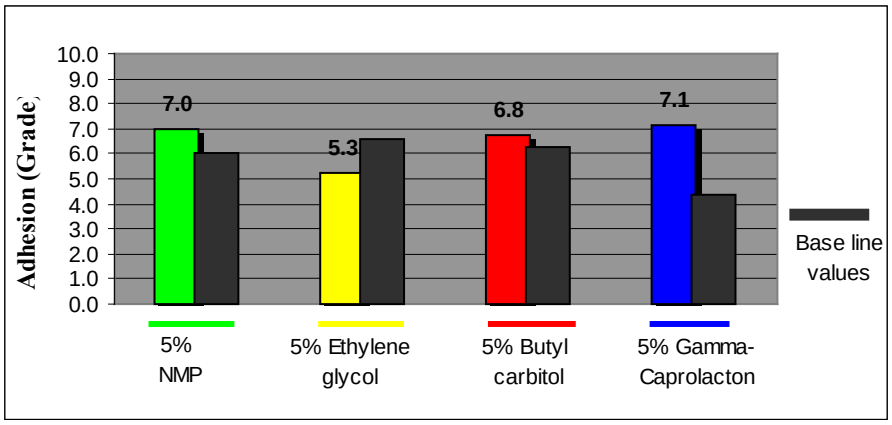


Figure (51) Effect of adding solvents on the Adhesion grade for ABS

Values illustrated in Figure 51 clearly indicate that examined samples generated almost same adhesion grade values as each other. These were slightly higher than base level results except with ethylene glycol which produced a lower adhesion level.

F- SEM Pictures (Grade)

Pictures were taken via SEM for ABS samples that have been treated by ultrasound with addition solvents and were graded visually. Grades compared to base line values are presented in Figure 51 as follows:

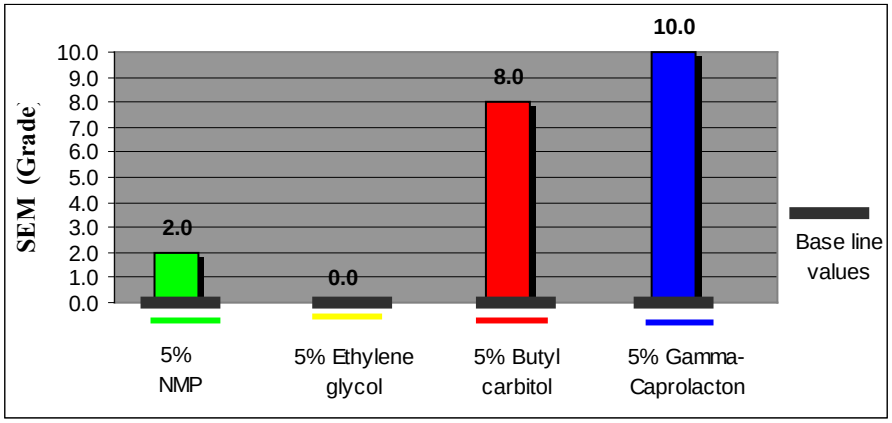
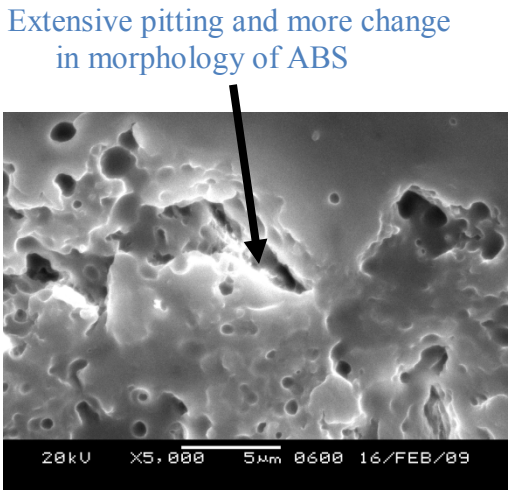


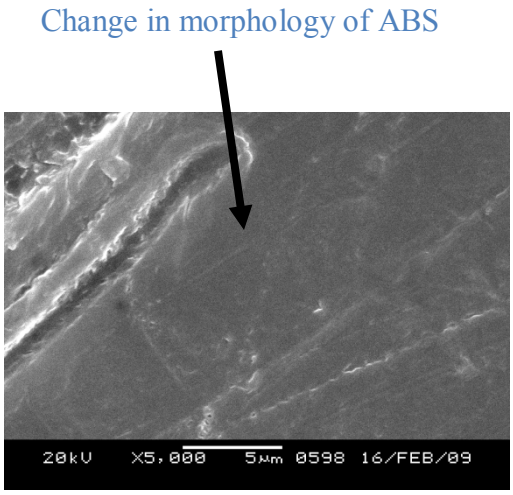
Figure (52) Effect of adding solvents on the SEM Pictures grade for ABS

It is easy to see from Figure 52 that utilizing 5 % gamma-caprolactone and 5 % butyl carbitol solvents have introduced the highest SEM values. Using NMP showed low SEM value while ethylene glycol solvent produced a surface without any change. Picture 28 shows ABS surface after ultrasonically treatment with 5 % gamma-caprolactone solvent while Picture (29) presents

ABS surface after ultrasonically treatment with 5 % butyl carbitol solvent. Both Pictures show a very obvious change in surface appearance after ultrasonically surface modification processes. It must be noticed that the base line values for adding solvent SEM grade have produced smooth surface with almost no texture surface (see figure 52).



Picture (28) ABS surface with 5 % of gamma-caprolactone at 0-2 °C



Picture (29) ABS surface with 5 % of butyl carbitol at 0-2 °C

4.3.4.1 Discussion

Initially, employing all types of solvent seems to have an influence on the ABS surface treatment compared to base line values which obtained with adding solvent control samples. It is easy to notice from the results obtained for adding the various solvents that utilizing a solution of 5 % gamma-caprolactone was the most effective solution to use as this produced a significant influence on the ABS surface treatment. This solvent was claimed to have good influence on the swellant step for epoxy surface modify processes applied with alkaline permanganate processes (Hirst *et al.* 2005). Although the surface of ABS is very glossy, the ultrasonic cavitation was effective in removing some amount of material from its surface as it is shown in Figure (47). The value for weight loss was approximately 0.1858 mg/cm^2. Almost the same value was obtained for weight loss when ABS is sonochemically treated with DI water only at low temperature (1848 mg/cm^2) but this result did not associated with good roughness, gloss meter, adhesion and SEM texture level results such as those achieved with gamma-caprolactone. The weight loss value is considered as being significant in contrast with the value obtained by Cobley and Mason

(2008) which was approximately 0.0200 mg/cm^2 and achieved at 40 ° C with 30 minutes ultrasonic treatment.

Highest roughness value was observed for ABS with gamma-caprolactone (Figure 49) which is the highest roughness value among all values in the previous experiments (section 4.3) and this was confirmed via obtaining a lower gloss meter value which confirms the roughness of the surface. Contact angle measurement (Figure 48) showed that a high reading is obtained with gamma-caprolactone which was somewhat similar to the value achieved with NMP solvent. Since the cavitation effect was recognized for its ability for erosion of the surface (Suslick and Price 1999), or chemically changing the surface via generation of free radicals which can oxidize the surface, a high rough surface could basically change the contact angle measurement via increasing the contact angle value rather than decreasing it (Ge, Turunen and Kivilahti 2003). In addition when gamma-caprolactone 5 % 9by volume) was added to DI water, this solvent was immiscible. It had formed globules in the solution which thereafter disappeared into the solution after 3-5 minutes after starting sonication process.

Adhesion data indicate that all solvents introduced a g ood level of adhesion in contrast with adhesion level that achieved for all previous experiments (section 4.3). It is obvious that the adhesion results obtained for base line value after adding solvents were higher than any adhesion level obtained in the previous ultrasonic experiments. Most interesting, the surface texture obtained for gamma-caprolactone was graded 10 (Figure 52) as it can be seen from Picture 28, the appearance of ABS surface has been changed from very smooth surface to new texture surface (extensive pitting and more change in morphology of ABS surface). Using butyl carbitol also produced a high textured surface but less than gamma-caprolactone one. It has been confirmed that lower temperature can increase the cavitation effects (Mason and Peters 2002: 9). Lowering temperature caused a decreasing on vapour pressure of water which already contained solvent with low vapour pressure. Consequently, it is suggested that in this case, the collapse of the cavitational bubbles is more violent when it hits the surface so more material is removed and more roughness surface is obtained and this secured a good mechanical bond producing good adhesion level for ABS.

4.3.5 Conclusion

ABS sonochemical surface modification processes indicates that the optimum power setting for surface modify this material was 100 W as at this power setting, low results were achieved with most of the analysis method which were better than other power settings which produced very poor results. Nevertheless, utilizing this power setting associated with a few problems which have been mentioned previously. Consequently, power settings of 50 a nd 80 W have been examined in low temperature experiments. Utilizing Power setting of 50 W at 0-10 °C has showed slightly more sonochemical influence rather than utilizing a power setting of 80 W at same temperature. Lowering the sonication temperature has been reported to enhance the cavitation effect (Mason and Peters 2002: 11). F reezing ABS samples before sonication processes has been examined and showed slightly better results compared to the base line values. Applying a power setting of 50 W at low temperature presented more significant results than freezing the samples. Adding solvents experiments revealed that significant results could be achieved when using a 5 % gamma-caprolactone compared to other results obtained at other different conditions. This might be attributed to some kind of chemical reaction occurring at the surface particularly as when this solvent is added to DI water, this solvent was immiscible. It must be taking into the account that using other solvents produced a good level of surface texture in addition to good adhesion levels compared to previous values.

4.4 NORYL MATERIAL SONOCHEMICAL SURFACE MODIFICATION

Noryl is a trade name for a type of plastic which is usually a blend of polyphenylene ether (PPE) and polystyrene. There are several types of Noryl and these depend on the proportion of PPE to polystyrene. This plastic is involved in many applications such as automotive instrument panels, computer components and interior components in electronic-electrical equipment. It has high glass transition temperature (Tg) and this was one of the reason for the printed circuit boards industries to use this type of plastic in addition to its other properties such as light weight, cheap and increased functionality and reliability. Alkaline permanganate has been used to surface modify this type of plastic (Pool *et al.* 2009) in addition to the Ozone surface modification method (Jobbins and Sopchak 1985). More recently, Noryl has been successfully surface treated

via sonochemical surface modification processes (Cobley and Mason 2007, Cobley and Mason 2008).

Several coupons of Noryl have been analysed via several methods in order to establish a base line value which ultrasonic results could be compared to. All the coupons were immersed in DI water for 15 minutes at 40 ºC and then all the analysis methods were utilized. The results are tabulated as following:

Weight loss (mg/cm^2)	Contact angle (θ)	Roughness (µm)	Gloss Meter %	Adhesion (Grade)	SEM (texture) (Grade)
0.0177	**95.9**	**0.5252**	**10.6**	**3.5**	**2.0**

Table 6, Base line value results for Noryl material

4.4.1 The optimization of power setting for sonochemical surface modification using Noryl material.

Experiments were carried out to determine the optimum power setting which could be useful for noryl material in the following experiments. The results obtained are exhibited as follows:

A- Weight loss

Results for weight loss at different power settings for noryl are exhibited in Figure (53) as follows:

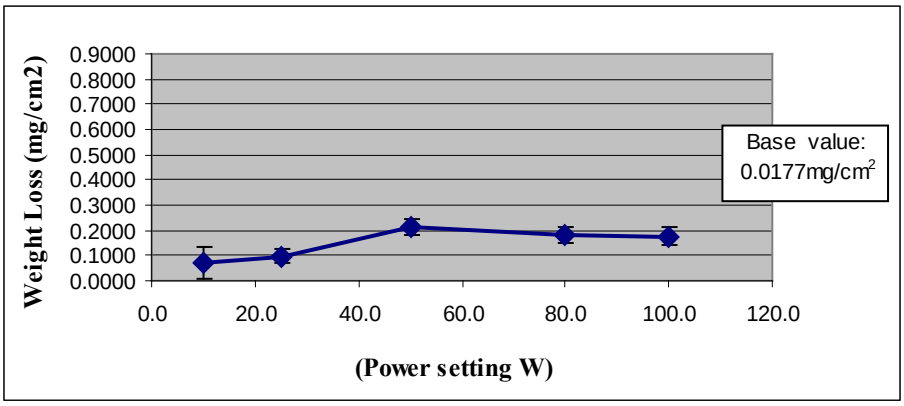


Figure (53) Weight loss for noryl material at different power settings

There is a clear indication that a slight high weight loss for noryl was achieved at power setting of 50 W and the values then decreased slightly at power setting of 80 and 100 W.

B- Contact angle

The contact angle values obtained for noryl at different power settings are shown as follows:

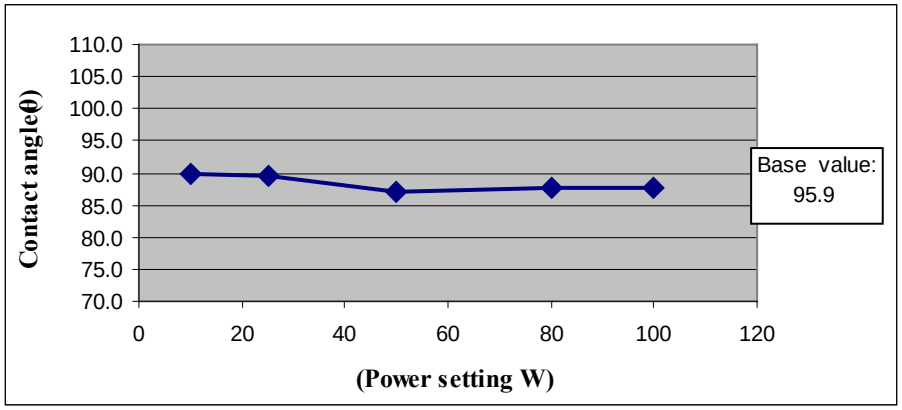


Figure (54) Contact angle for noryl material at different power settings

Data from above figure shows a dropping in the contact angle values particularly at 50 W presenting the lower contact angle value. The value slightly increased at the power settings of 80 and 100 W sequentially.

C- Roughness

Results achieved for noryl roughness measurements are presented in Figure 55 as follows:

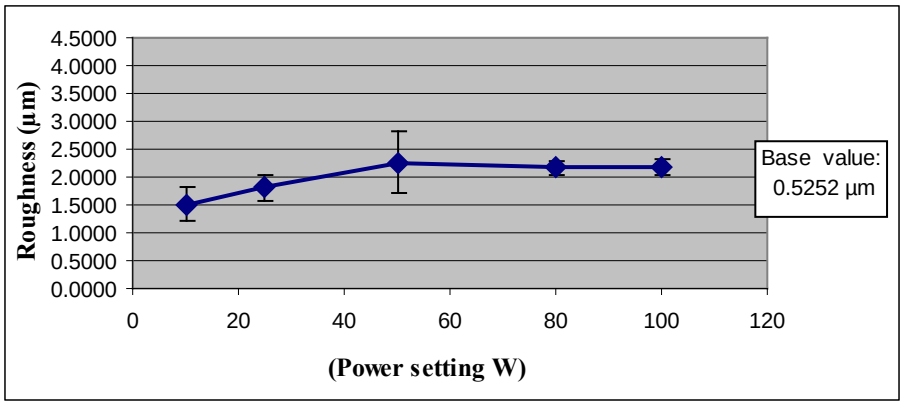


Figure (55) Roughness for noryl material at different power settings

Results show that a higher value of roughness for noryl was obtained at a power setting of 50 W. Power settings of 80 W and 100 W produced slightly lower roughness reading.

D- Gloss meter readings

Gloss meter data for noryl at different power settings are shown in Figure 56 as follows:

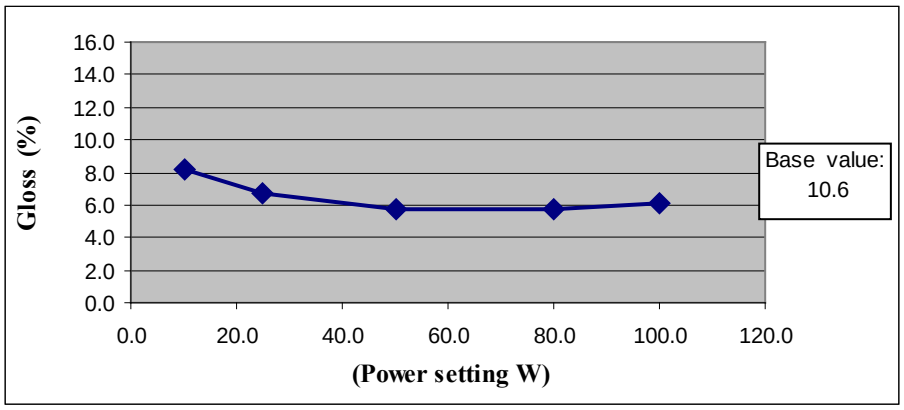


Figure (56) Gloss meter readingsfor noryl material at different power settings

Results indicate that the minimum value of gloss meter occurred at 80 and 50 W. The values increased a little when power setting was increased to 100 W.

E- Adhesion (Grade)

Adhesion levels for samples at different power setting have been assessed visually and the values which achieved are exhibited as follows:

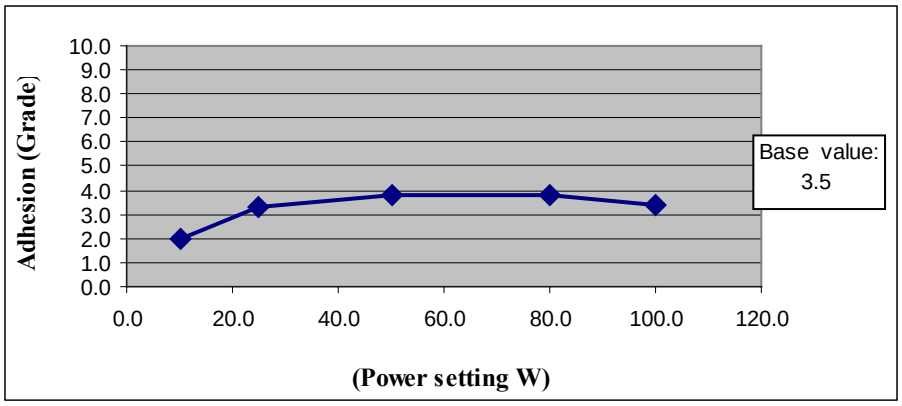


Figure (57) Adhesion grade for noryl material at different power settings

Figure 57 indicates that adhesion levels for noryl material were low at different power settings. The adhesion increases with increasing the power settings until reaching a higher value at 50 and 80 W and the adhesion somewhat dropped at 100 W.

F- SEM Pictures (Grade)

SEM pictures have been assessed visually and each picture has been given a grade. The results are shown in Figure 58 as follows:

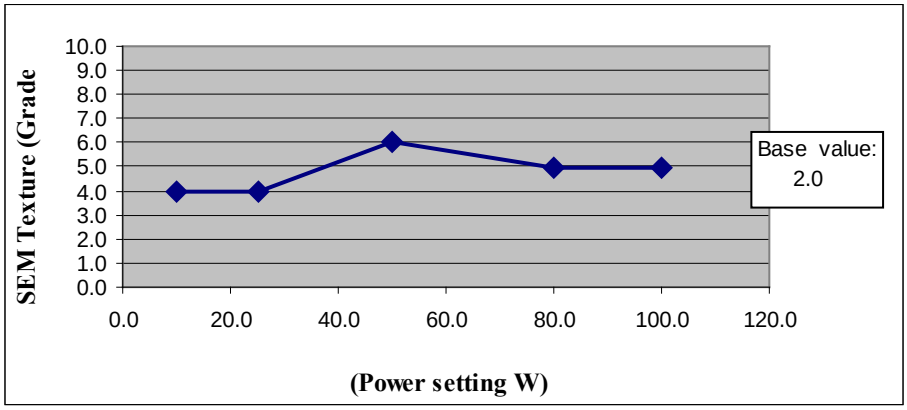
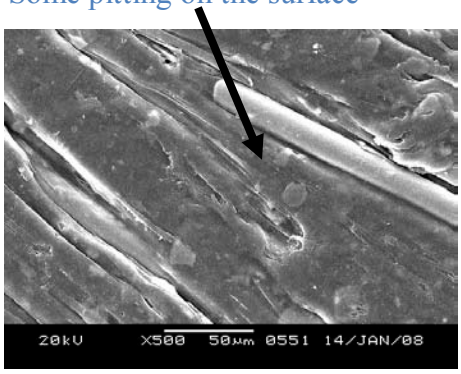


Figure (58) SEM Pictures (Grade) for noryl material at different power settings

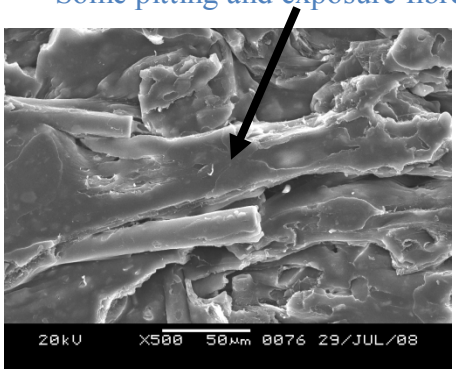
Higher texture grade was produced when a power setting of 50 W is used. Other power setting for ultrasound treatment gave lower grades.

Some pitting on the surface



Picture (30) Noryl material before treatment

Some pitting and exposure fibre



Picture (31) Noryl material surface at 50 W at 40 ºC

4.4.1.1 Discussion

It is obvious that ultrasonic treatment has a significant impact on the noryl surface modification even at a low power setting (10 W) in contrast to base line values and ultrasound impact observed for all the types of surface analysis methods employed (see above figures). For example at a power setting of 10 W the sample weight loss was 0.0710 mg/cm^2 and this is much higher than the base value weight loss of 0.0177 mg/cm^2. Nevertheless, the highest weight loss is obtained at power setting of 50 W which was 0.2113 mg/cm2. A power setting of 50 W has also

produced the lowest contact angle value meaning the chemistry of the surface has been changed more at this power setting compared to the others. The changes in the contact angle due to the application of ultrasound were also confirmed by Price, Keen and Clifton (1996) suggesting that an oxidation reaction is occurring at the polymer surface.

Moreover, roughness (Figure 55) and gloss meter readings (Figure 56) showed very good correlation with each other with the highest roughness occurring at 50 W and low gloss meter value observed at the same power setting although a low gloss meter value also obtained at 80 W. Adhesion (Figure 57) showed somewhat higher adhesion level at 50 W which was almost the same adhesion level achieved at 80 W. High surface morphology is produced at power setting of 50 W and this was expected as the higher roughness value obtained at this power setting. There is a c lear indication that at 50 W, the cavitation effect is maximized and the microjetting influence is more in addition to the free radicals activity which seems to be more at this power setting due to more chemistry changing produced at the surface. In spite of the fact that a power setting of 80 W produced values close to those achieved at 50 W in term of roughness, gloss meter and adhesion level at this power setting the temperature increased quickly compared to other power settings and it is known that at high temperatures the cavitation effects are reduced (Mason and Peters 2002: 9). This reduction is attributed to the bubbles that contain more vapour pressure at high temperature which will be cushioned on collapse leading to less violent collapsing so the cavitational effect is decreased.

So, the optimum power setting is clearly at 50 W as good results were achieved with most of the analysis methods therefore this power setting was used in the following experiments.

4.4.2 Effect of low temperature on the sonochemical surface modification of Noryl

The optimum power setting of 50 W has been examined at a starting temperature of 0 ºC for all the following experiments (section 4.4). The ultrasonic intensity measurement for this power setting at this low temperature has indicated that the ultrasonic intensity for this input is slightly changed (Table2).

A- Weight loss

In Figure 59, the results for weight loss for noryl at low temperature compared to the weight loss at 40 ºC are shown as follows:

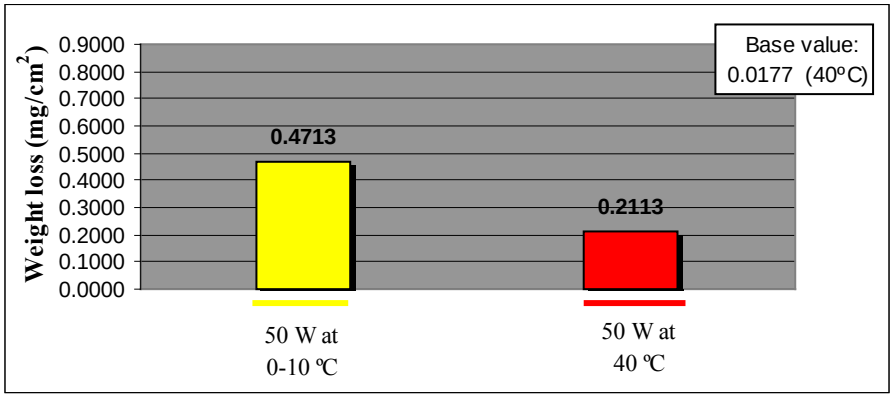


Figure (59) Effect of low temperature on weight loss for Noryl material

The results clearly indicate that the greatest material removed at the surface was observed at power setting of 50 W at 0 ºC compared to 50 W that obtained at 40 ºC.

B- Contact angle

Contact angle values at low temperature for noryl are shown in Figure 60 and compared to the values observed at 40 ºC for the same power setting. The results are exhibited as follows:

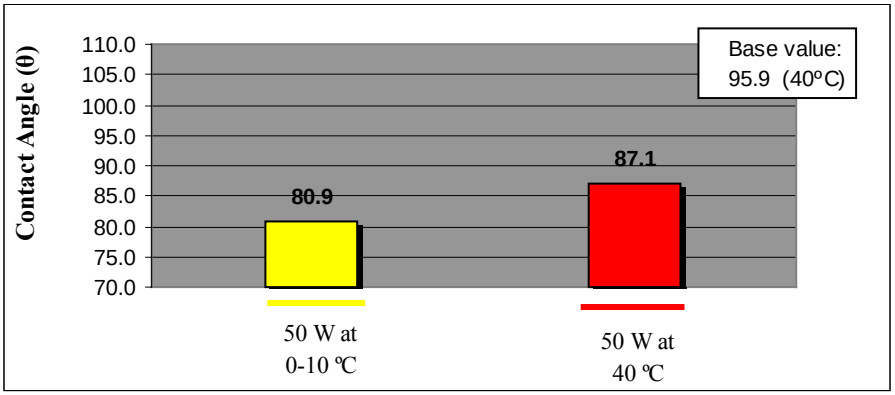


Figure (60) Effect of low temperature on contact angle for noryl material

The results confirm that the chemistry of the surface is changed when 50 W is used at 0 ºC compared to the same power setting used at 40 ºC.

C- Roughness

The roughness data obtained at low temperature and compared to same power setting used at 40 ºC are presented in Figure 61 as follows:

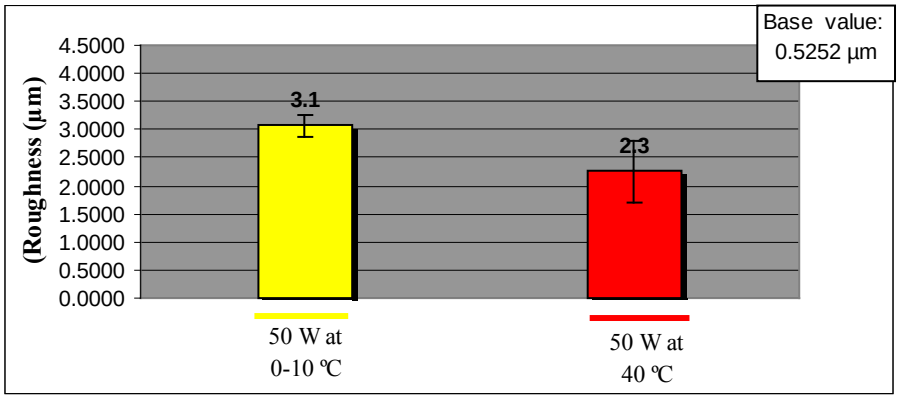


Figure (61) Effect of low temperature on roughness for noryl material

The results obtained in Figure 61 revealed that 50 W at 0 ºC produced higher roughness readings while same power setting at 40 ºC gave lower reading.

D- Gloss meter readings

Gloss meter results for noryl for low temperature experiments compared to same power setting at 40 ºC are shown in Figure 62 as follows:

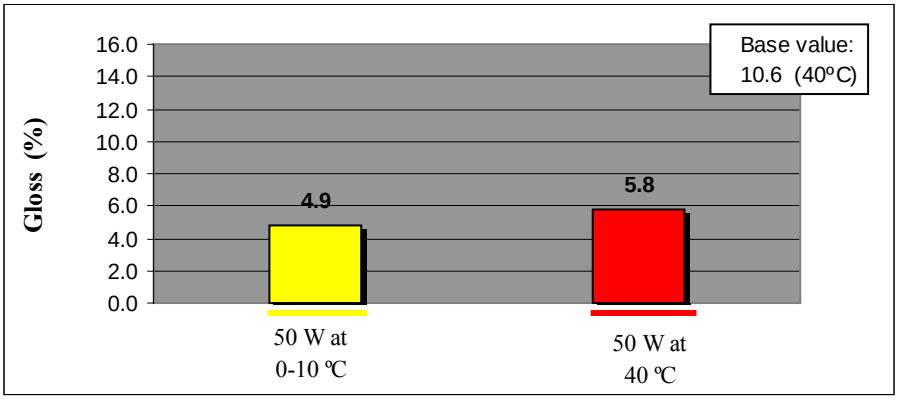


Figure (62) Effect of low temperature on Gloss meter readings % for noryl material

50 W at 0 ºC produces lower gloss meter reading. Generally the result at high temperature is higher to that obtained for same power setting at 0 ºC.

E- Adhesion (Grade)

Adhesion level for low temperature experiments for noryl have been assessed visually and compared to the results observed at 40 ºC for the same power setting. The results are shown in Figure 63 as follows:

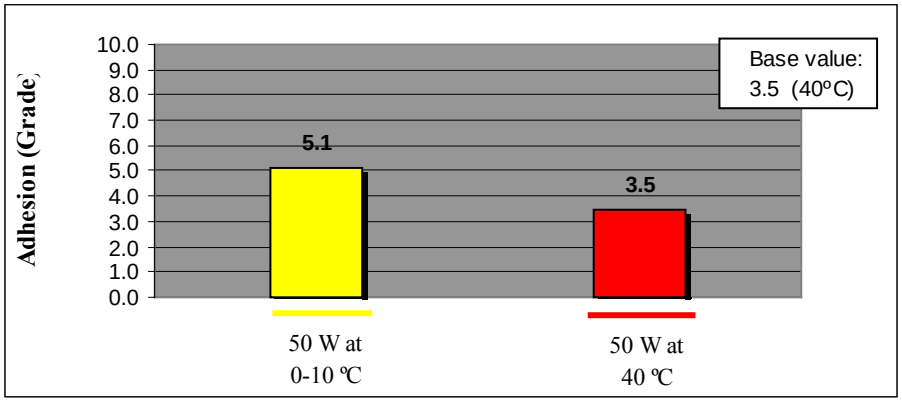


Figure (63) Adhesion grade for Noryl material at low temperature

The above data indicates that the adhesion has a good value when employing a power setting of 50 W at 0 ºC.

F- SEM Pictures (Grade)

Pictures were taken via SEM and were graded visually. Grades are compared to the values obtained at 40 ºC for the same power setting and presented in Figure 64 as follows:

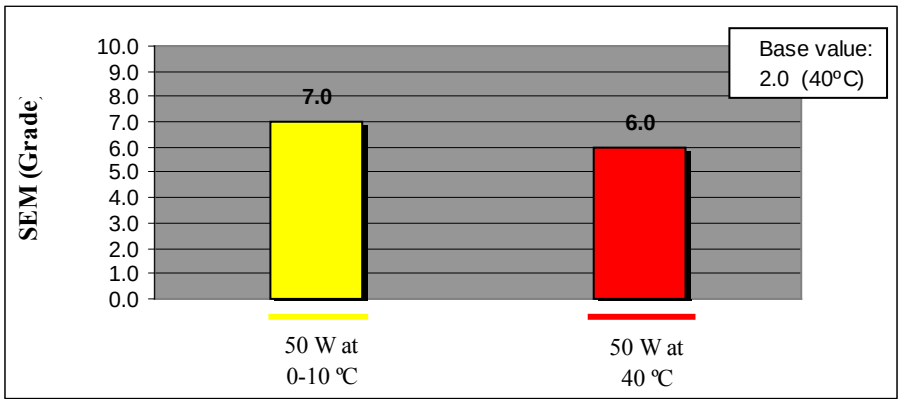
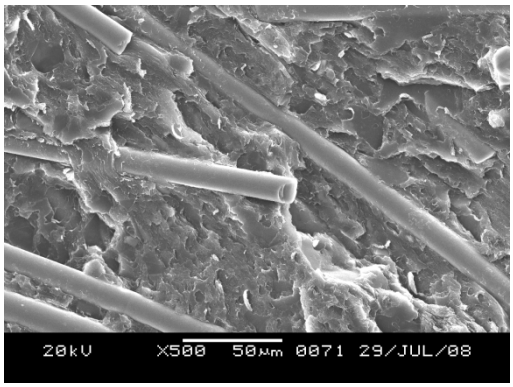


Figure (64) SEM Pictures (Grade) for Noryl material at low temperature

These results clearly indicate that lowering the solution temperature caused a slight incease in the texture grade at 50 W where the temperature is 0-10 °C in contrast to the value obtained at 40 ºC. SEM Picture (32) showed a good morphology surface generated at low temperature compared to surface before treatment (Picture 30).



Picture (32) Noryl surface at 50 W at 0-10 °C

4.4.2.1 Discussion

Observing all the results obtained gives an easy decision that lowering the sonication temperature has enhanced the cavitation effect compared to the values produced at 40 °C. The weight loss value (0.4713 mg/cm^2) obtained at power setting of 50 W at 0 °C is higher (double) in contrast with value obtained when 50 W is used at 40 °C (0.2113 mg/cm^2) and it is very high than weight loss results obtained via Cobley and Mason (2008) which was approximately 0.1000 mg/cm^2 a nd 0.0780 mg/cm^2 which obtained by Cobley and Mason (2007). Utilizing 0 °C caused a d ecrease in contact angle values reflecting a change in the chemistry of the noryl surface and utilizing same temperature has shown a significant higher roughness value and this fact was confirmed via SEM grade value (Figure 64). Gloss meter results correlated with the roughness results suggesting a rougher surface is produced at low temperature. Adhesion level is higher at low temperature because of the rougher surface more chemical changes at the surface which provide a more mechanical and chemical bond between the noryl surface and subsequent electroless plating.

Increased cavitation effects can be achieved via lowering the temperature (Mason and Peters 2002: 9). This effect could be caused by the increased viscosity of water or decrease the low vapour pressure of water at low temperature (Mason and Peters 2002: 11). As a consequence, the collapse of the cavitational bubbles is more violent when it hits the surface removing more material so rougher surface is obtained.

4.4.3 Effect of frozen samples on the sonochemical surface modification of Noryl

Samples from noryl material were placed in the freezer at -2 to 0 ºC for up to 24 hours and then treated via ultrasound at starting temperatures approximating 0 ºC and 40 ºC. A power setting of 50 W was utilized for all the experiments (see section 3.8). The results achieved in this section were compared to those obtained previously at the same conditions (50 W at 40 ºC and 0 ºC) without freezing. Results are as follows:

A- Weight loss

Weight loss values achieved for noryl frozen samples compared to not frozen samples at the same conditions are shown in Figure 65 as follows:

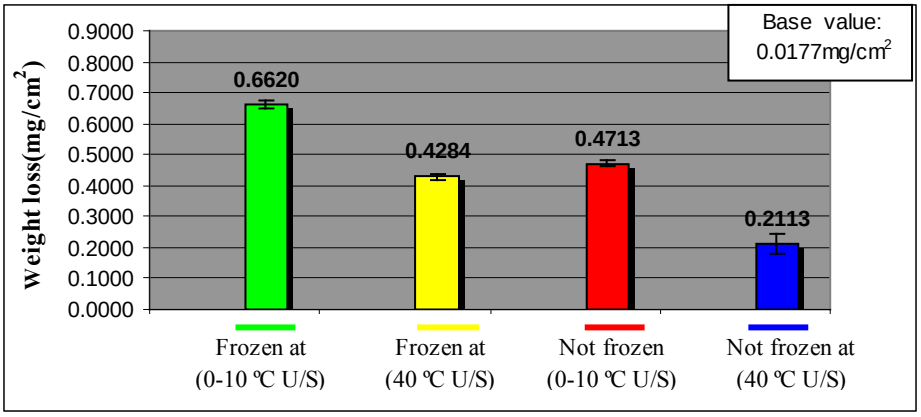


Figure (65) Effect of freezing samples on weight loss for noryl material

Frozen samples ultrasonically treated at 0 ºC had a big impact as highest material is removed from the surface. Applying low temperature for ultrasonically treat non-frozen samples at a power setting of 50 W produced a weight loss value higher than value for frozen samples at 40 ºC.

B- Contact angle

In Figure 66, results for contact angle measurements for frozen samples are exhibited and compared to not frozen samples under the same conditions as follows:

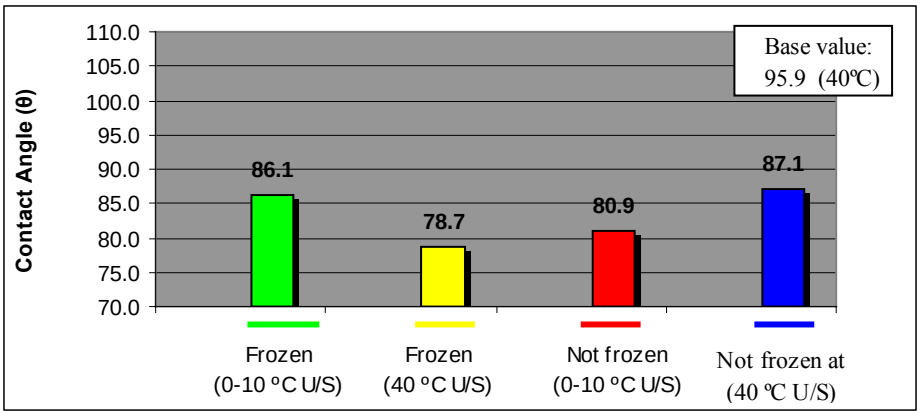


Figure (66) Effect of frozen samples on contact angle for noryl material

The lowest value for contact angle is observed with samples that were frozen and ultrasonically treated at 40 ^{o}C compare to other values obtained at different conditions. Employing low temperature and a power setting of 50 W with non-frozen samples also introduced low contact angle reading.

C- Roughness

Roughness results achieved for frozen samples compared to not frozen samples at same conditions are presented in Figure 67 as follows:

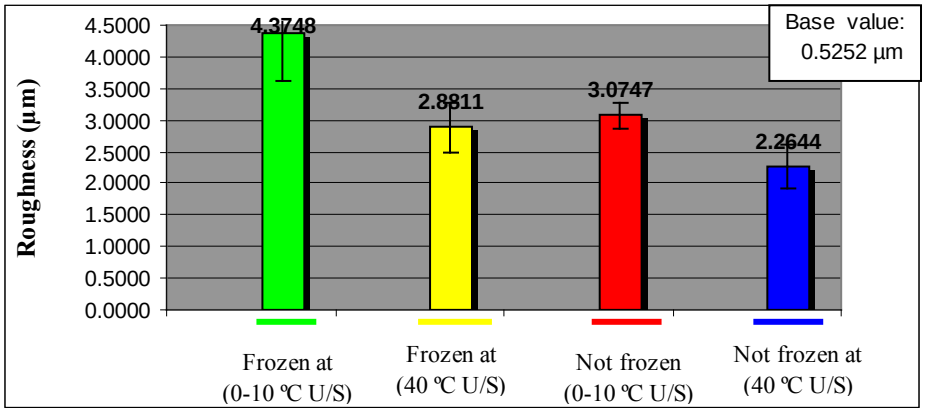


Figure (67) Effect of frozen samples on roughness for noryl material

Higher roughness value was observed for samples that were frozen and ultrasonically treated with a power setting of 50 W at 0-10 ^{o}C. Other conditions produced lower values.

D- Gloss meter readings

In Figure 68, gloss meter values for frozen samples are compared to not frozen samples under the same reaction conditions are shown as follows:

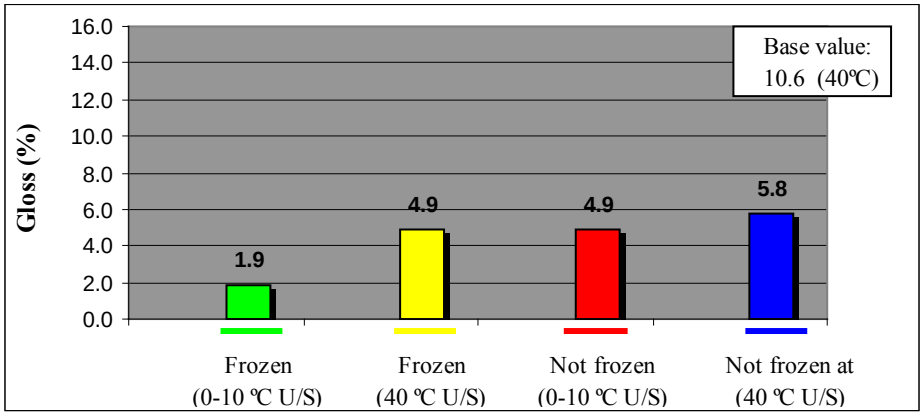


Figure (68) Effect of frozen samples on gloss meter readings for noryl material

The lowest value for gloss meter is achieved for samples which are frozen and treated at 0 ^{o}C compared to other values obtained at various conditions.

E- Adhesion (Grade)

Adhesion levels for the frozen samples have been assessed visually and are compared to results achieved for not frozen samples under the same conditions. Results are presented in Figure 69 as follows:

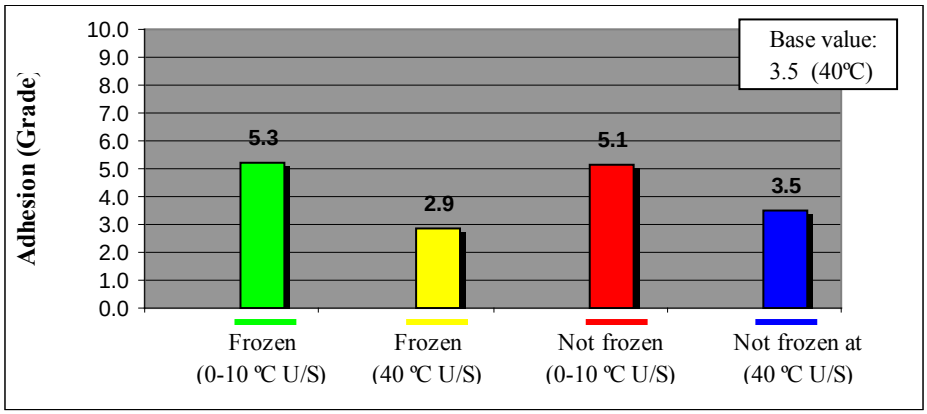


Figure (69) Adhesion grade for noryl material frozen samples

The highest level of adhesion is seen with the frozen samples at 0 ^{o}C which almost the same for not frozen samples at low temperature.

F- SEM Pictures (Grade)

Scanning electron microscope pictures have been assessed and each picture has been given a grade. Grades are shown in Figure 70 as following:

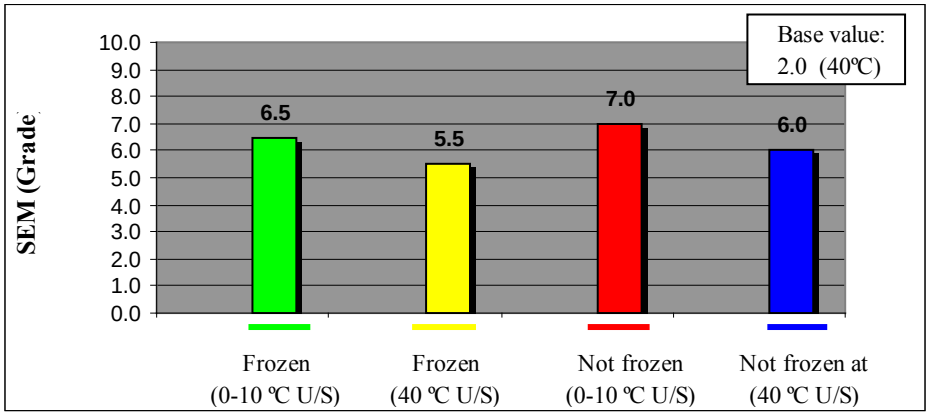
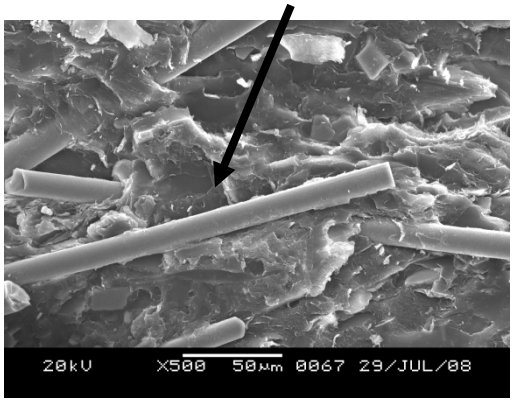


Figure (70) SEM Pictures (Grade) for noryl material frozen samples

Highest surface texture obtained when samples were not frozen at 0 ^{o}C. Freezing samples at 0 ^{o}C produced a slightly lower texture grade. SEM Picture (33) for frozen samples at low temperature produced a surface with exposed glass and high morphology.

Further exposure fibre and more change in morphology of Noryl



Picture (33) Frozen noryl surface ultrasonially treated with 50 W at 0-10 °C

4.4.3.1 Discussion

The outcome of the frozen samples experiments revealed that freezing noryl associated with low temperature ultrasonic treatment showed a significant effect on the surface modification processes. Highest weight loss (Figure 65) and roughness (Figure 67) value has been achieved for frozen samples at 0 °C compared to other conditions. This has been confirmed via lower

gloss meter measurements (Figure 68) which refer to an increased rougher surface. Contact angle value 86.1 (Figure 66) obtained for frozen samples at 0 °C was the higher value among other circumstances suggesting that no chemistry changes occurred at the noryl frozen surface. It was reported that a very rough surface could introduce an increasing in contact angle values which indicates to the surface roughness rather than the chemistry of surface (Ge, Turunen and Kivilahti 2003). Adhesion data (Figure 69) showed that the adhesion level for frozen samples treated at 0 °C was slightly higher than not frozen samples sonicated at 0 °C. SEM (Figure 70) results indicated that in spite of the frozen samples producing good results in term of adhesion and texture level, not frozen noryl plaques at 0 °C produced somewhat higher SEM level.

These results are also considered to being remarkable results in contrast with results obtained by Cobley and Mason (2008) (utilizing 30 minutes and at 40 ° C), such as weight loss obtained: approximately 0.1000 mg/cm^2 and roughness was approximately 0.2500 µm while for frozen samples at 0 °C value is 0.6620 mg/cm^2 for weight loss and 4.3748 µm for roughness. It has been mentioned previously that from an economic point of view, freezing samples would introduce an additional step for surface modification processes which means that processes will be longer.

4.4.4 Effect of adding solvents on the sonochemical surface modification of Noryl

Samples of noryl material have been sonochemicaly surface modified with four solvent solutions. A 5 % (volume) solution for each solvent has been prepared (see 3.9) and the sonochemical processes applied with optimum power setting of 50 W at a starting temperature of 0 ºC for all the following experiments. The results obtained for sonochemical experiments compared to the base line value for adding solvent (control samples) are shown as follows:

A- Weight loss

Figure 71 shows the results achieved for addition of solvents on the weight loss of noryl. Results under ultrasonic treatment compared to the base line values (for adding solvents) are shown as follows:

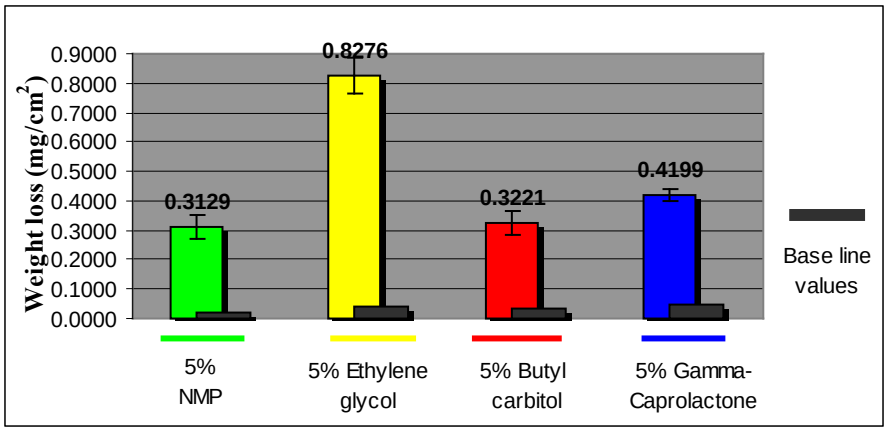


Figure (71) Effect of adding solvents on the weight loss for noryl material

There is a clear indication from Figure 71 that the highest weight loss for noryl was achieved when a 5% of ethylene glycol solvent was used for ultrasonically treatment. Gamma-caprolactone produced higher weight loss value in contrast with NMP and butyl carbitol solvents.

B- *Contact angle*

Contact angle data which was obtained for the effect of ultrasound on addition of solvents in contrast with base line values are presented as follows:

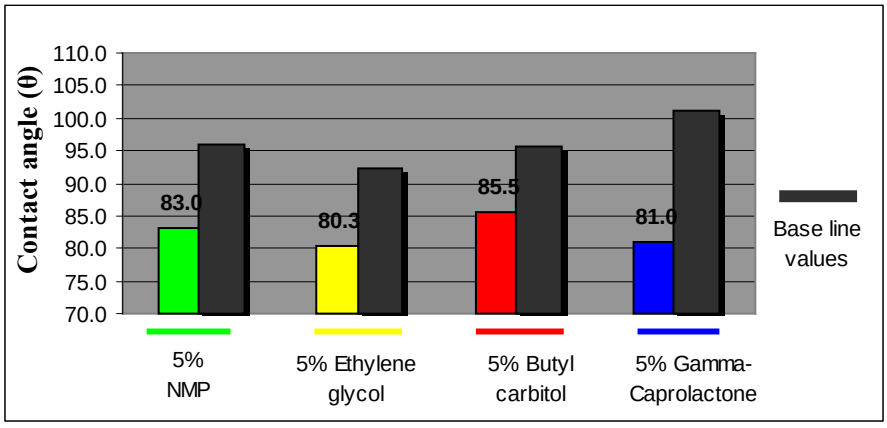


Figure (72) Effect of adding solvents on the contact angle for noryl material

The lowest value for contact angle is observed for samples that are treated ultrasonically with 5% ethylene glycol solvent which was very close to the value obtained with Gamma-caprolactone. Results for the other solvents are not as good but are still close to each other and still produced a lower contact angle reading than the base line reading.

C- Roughness

The roughness results achieved by using different solvents with ultrasound compared to base line values are exhibited as follows:

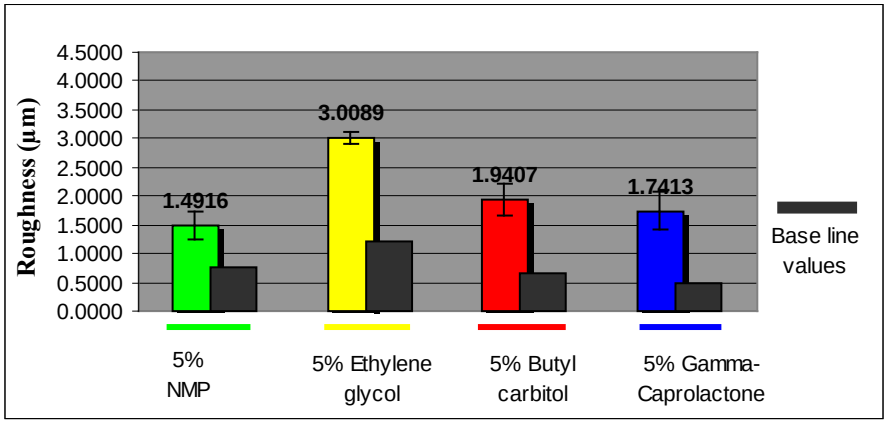


Figure (73) Effect of adding solvents on the roughness for noryl material

A higher roughness value is achieved when a 5 % of ethylene glycol solvent is added compared to other solvents result which still produced values higher than base line results.

D- Gloss meter readings

The influence of adding solvents on the gloss meter % for noryl material compared to the base line values for same solvents are presented in figure 74 as follows:

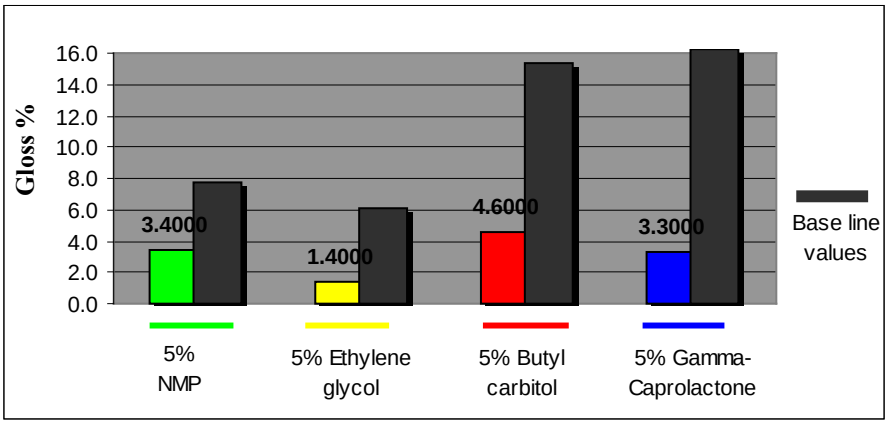


Figure (74) Effect of adding solvents on the gloss meter readings for noryl material

It is obvious that utilizing ethylene glycol introduced the lowest gloss meter reading, NMP and gamma-caprolactone gave almost similar gloss meter readings. Butyl carbitol produced the highest reading. All added solvents introduced lower values than base line values.

E- Adhesion (Grade)

Adhesion level has been assessed visually for samples treated under additional solvent conditions. Results compared to base line results are shown in Figure 75 as follows:

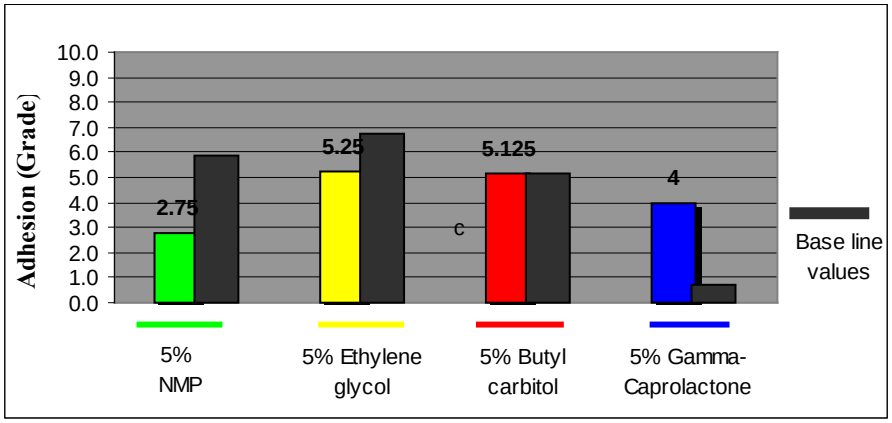


Figure (75) Effect of adding solvents on the Adhesion grade for noryl material

Values for adhesion indicate that samples treated with ethylene glycol produced higher value compared to other solvents remarking that using butyl carbitol produced a slightly lower value. In spite of this fact, adhesion level for the three solvents were the same or less than base value except with gamma-caprolactone which showed higher value than base line one.

F- SEM Pictures (Grade)

Pictures were taken via SEM and were graded visually for adding solvent experiments. Grades are presented in Figure 76 as follows:

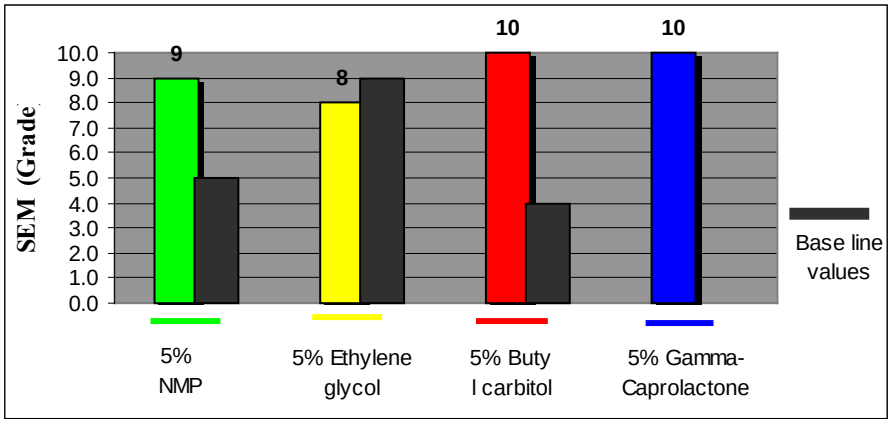
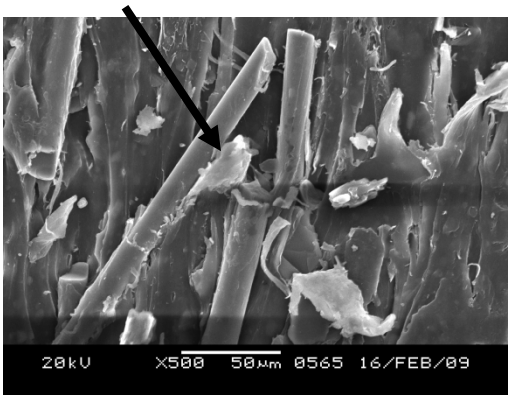


Figure (76) Effect of adding solvents on the SEM Pictures grade for noryl material

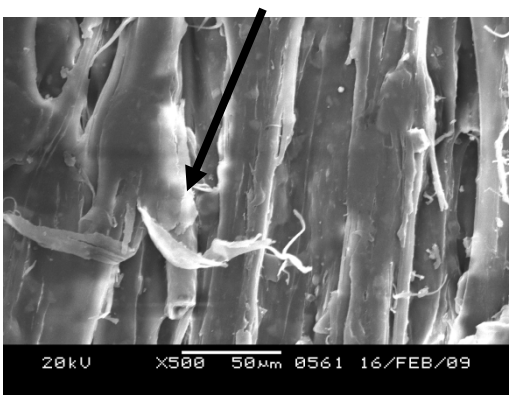
It is easy to see from Figure 76 that utilizing either 5 % gamma-caprolactone or 5 % butyl carbitol solvents have produced the highest SEM values. Using NMP showed less SEM value. Moreover, Picture (34) shows noryl surface after ultrasonically treatment with 5 % of ethylene glycol while Picture (35) presents noryl surface after ultrasonically treatment with 5 % Gamma-caprolactone solvent. It must be noticed that the base line values for adding solvent SEM grade have produced smooth surface with almost no texture surface with Gamma-caprolactone solvent.

Extensive exposure fibre



Picture (34) Noryl surface with 5 % of ethylene glycol at 0-2 °C

Extensive exposure fibre



Picture (35) Noryl surface with 5 % of gamma-caprolactone at 0-2 °C

4.4.4.1 Discussion

Results obtained in the above experiments indicate that utilizing 5% (volume) ethylene glycol resulted in a very high weight loss reading compared to other adding solvents (Figure 71). Ethylene glycol has low vapour pressure and this could enhance the cavitation effect (Mason & Peter 2002: 9). Highest roughness value (Figure 73) was observed with ethylene glycol and this has been confirmed via the lowest gloss meter reading (Figure 74) obtained with this solvent suggesting that the noryl surface has been changed to be more roughened. The contact angle results (Figure 72) produced almost the same noryl surface with all solvents with the lowest contact angle value achieved with ethylene glycol. Adhesion data (Figure 75) showed that ethylene glycol produced the higher adhesion level but, this level was less than the base line value obtained with the added solvent samples. The reason behind the low adhesion level might be due to a very high rough surface associated with this particular solvent which produced more exposed glass (Picture 34) and this could be considered as a reason in lowering the adhesion level due to possible surface debris (Cobley and Mason 2008). Ethylene glycol solvent is used

widely within the printed circuit boards companies as a swellant solvent (Goosey and Poole 2004) and in Asian countries in the printed circuit board industries (LaDou 2006).

Butyl carbitol solvent introduced good results in term of SEM (Figure 76) and adhesion (Figure 75) but, it produced a less significant value for weight loss, roughness, contact angle and gloss meter in contrast with ethylene glycol values. Overall outcomes of adding solvent experiments for noryl revealed that utilizing ethylene glycol solvent was the most efficient solvent among other solvents as with this solvent as a good results of weight loss, roughness, gloss meter contact angle and adhesion level were associated with this solvent.

4.4.5 Conclusion

Noryl sonochemical surface modification processes clearly indicates for a power setting of 50 W as the optimum power setting for surface modification of this material. Using this power setting produced good results via all analysis methods. Consequently, a power setting of 50 W has been examined in low temperature experiments. Utilizing Power setting of 50 W at 0-10 °C has introduced more sonochemical influence rather than utilizing the same power setting at 40 °C. Decreasing the sonication temperature increases the cavitation effect particularly increasing the microjetting effects. Noryl frozen samples sonicated with power setting of 50 at 0 °C have showed noteworthy results compared to the base line values and low temperature values except for SEM results which were slightly lower. Adding solvents experiments revealed that significant results, in contrast with most of previous results, are achieved if a 5 % ethylene glycol is used. Utilizing other solvents produced a good level of surface texture levels compared to previous values.

4.5 SONOCHMEICAL SURFACE MODIFICATION OF CERAMIC MATERIAL

Ceramic is an inert chemical material which has widespread use in electronic components for telecommunication purposes, aerials and antennas. This wide usage is because of many reasons such as the high resistant nature of this material to heat and to corrosive environment in addition to its electrical properties. This material has been traditionally surface modified using a mixture contained concentrated hydrofluoric acid (Shi *et al.* 1997). Ultrasound has been indicated to have

the ability to surface modify this material (Cobley and Mason 2007). Ceramic plaques were analysed via several techniques in order to establish a base line value which ultrasonic results could be compared to. All plaques were immersed in DI water for 15 minutes at 40 ºC and then all the analysis techniques described in section (3.10) were utilized except the contact angle and gloss meter methods, due to the fact that the ceramic has a cylinder shape which could not be fitted into the equipment used with these techniques. The results of all the tests in Table (7) are as follows and are the average values of three repeat tests:

Weight loss (mg/cm^2)	Roughness (µm)	Adhesion (Grade)	SEM (texture) (Grade)
0.0024	**0.4598**	**1.9**	**0.0**

Table 7, Base line value results for ceramic material

4.5.1 The optimization of power setting for sonochemical surface modification using Ceramic material.

Experiments were carried out to choose the optimum power setting which could be useful for ceramic material in the following experiments. The results obtained are presented as follows:

A- Weight loss

Weight loss results for ceramic at different power settings are as follows:

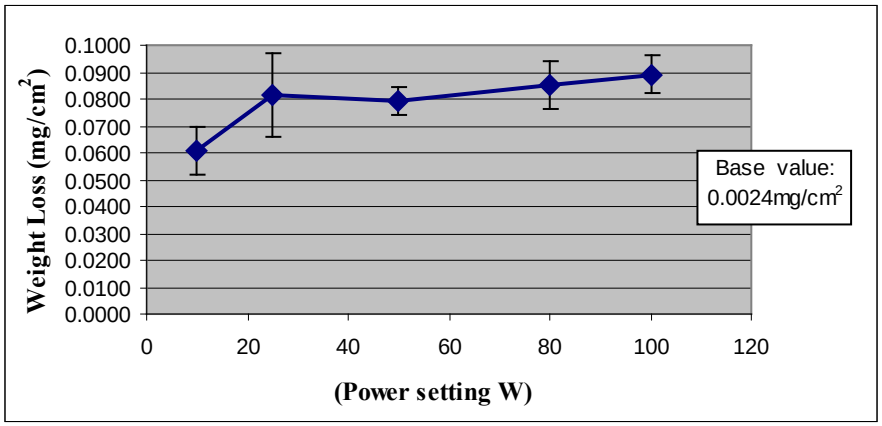


Figure (77) Weight loss for ceramic material at different power settings

Figure 77 indicates that weight loss increases with increasing the power settings. Higher removed material was achieved at power setting of 100 W.

B- Roughness

Roughness values for ceramic at different power settings are shown as follows:

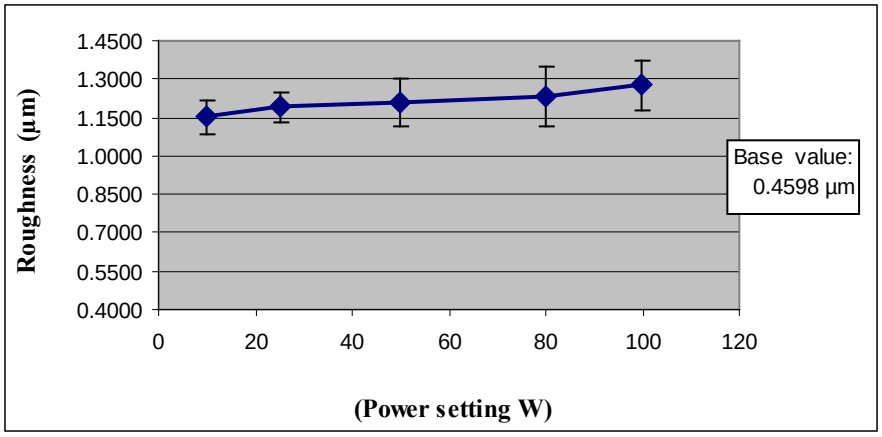


Figure (78) Roughness for ceramic material at different power settings

Results indicate that a higher value for roughness is obtained at a power setting of 100 W. Roughness increase with increasing power setting.

C- Adhesion (Grade)

Adhesion level for ceramic plaques at different power settings have been assessed visually and the values are exhibited as follows:

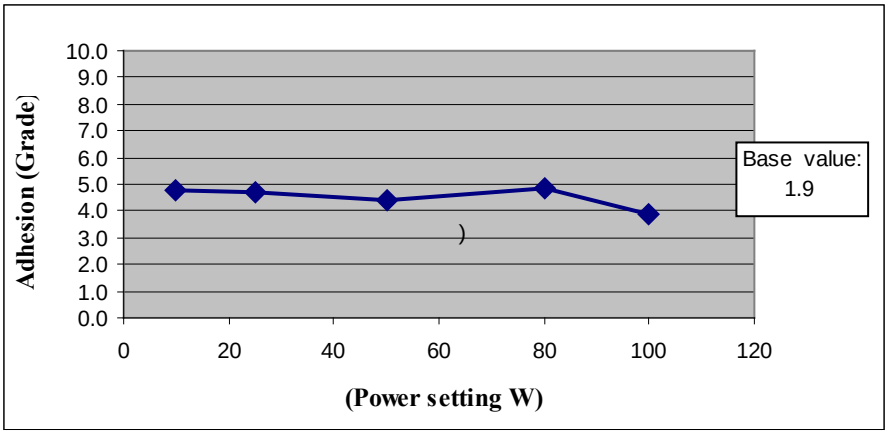


Figure (79) Adhesion grade for ceramic material at different power settings

Figure 79 indicates that the adhesion level was almost same or closes for different power settings (grades between 4-5). An 80 W has produced somewhat higher weight loss value in contrast to other power settings.

D- SEM Pictures (Grade)

SEM pictures for different power setting have been assessed and each picture has been given a grade. The results are shown as follows:

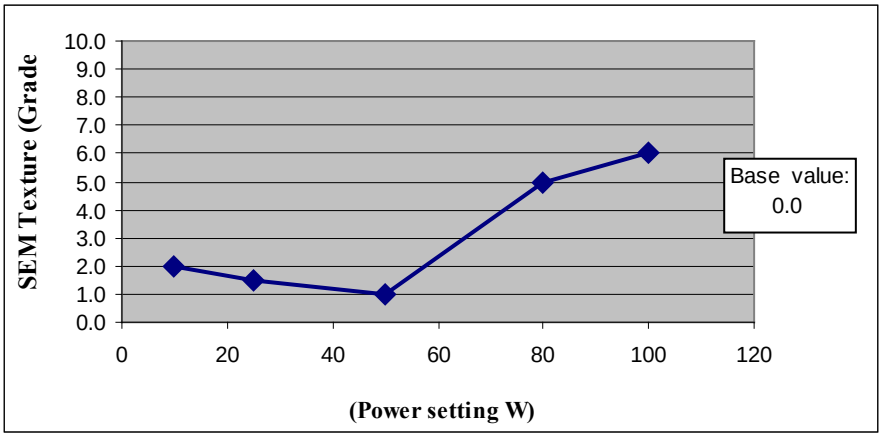
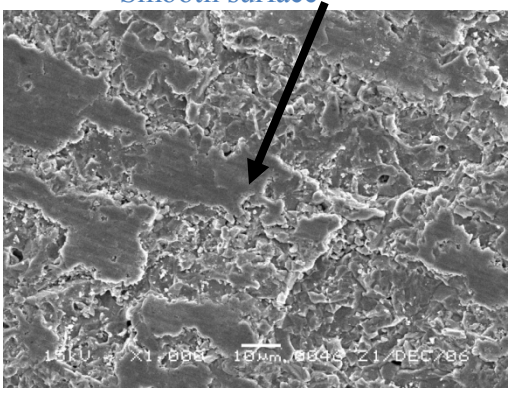


Figure (80) SEM Pictures (Grade) for ceramic material at different power settings

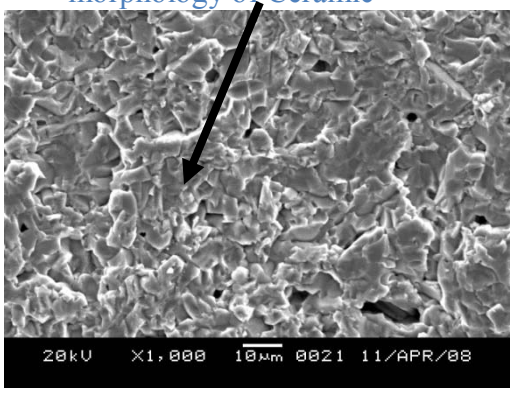
It easy to see (figure 80) that higher texture grade is produced when a power setting of 100 W is used. Utilizing a power setting of 80 W has also produced high grade, but less than the value achieved at 100 W. Other power settings produced lower texture grades. Furthermore, Picture (37) shows a surface morphology of ceramic at 100 W while Picture (36) shows ceramic plaque before treatment.

Smooth surface



Picture (36) Ceramic material before treatment

Extensive pitting with change in morphology of Ceramic



Picture (37) Ceramic material surface at 100 W

4.5.1.1 Discussion

Weight loss results for ceramic material after applying power ultrasound showed an increasing with an increase in the power settings. A slight increasing in weight loss is observed at 100 W. (Figure 77). A weight loss for ceramic types was observed when a traditional fluoroboric acid is used as etchant with a small concentration of nitric acid (Baumgartner 1989). Roughness values correlated with weight loss results as the surface roughness increased when the power setting is increased reaching a maximum roughness value of 1.2752 µm at 100 W (Figure 78). The adhesion data (Figure 79) conflicted somewhat with the results of other analysis methods. Although the adhesion levels obtained for different power setting were somewhat close to each other. The most remarkable value was the low adhesion level observed at 100 W which was expected to introduce higher adhesion value due to high roughness and weight loss results obtained at 100 W. It seems that achieving high roughness surface for ceramic material may introduce a low adhesion level and this might be due to debris at the surface or changing the surface which prevent a good adhesion to be obtained. Generally, applying ultrasound to surface modify a ceramic showed a significant influence compared to base line value even if a lower power setting of 10 W is utilized (see above figures).

In contrast with results which obtained for ceramic by Cobley and Mason (2007), these results also be considered as being significant as the values obtained at this project were more higher than results obtained by Cobley and Mason such as roughness value which was approximately 0.3800 µm while current value is 1.2752 µm at 100 W. It is apparent from Picture 36 and 37 that the surface of the ceramic before treatment has some type of smearing layer and this surface after being ultrasonically treated at 100 W produced a more textured surface by removing the smearing layer. The most convenient power setting to treat ceramic samples seems to be 100 W where weight loss, higher roughness and SEM values are obtained. In spite of this fact, it has been mentioned previously that at 100 W a greater amount of water is required and the temperature of the process increases very rapidly and the general effects of the cavitation are reduced (Mason and Peters 2002: 9). Consequently an extra amount of water is required to cool down the system. In addition the efficiency of the probe is reduced. It mentioned previously that after 5-6 minutes from starting of the process the power deceases down to 85 W which is near the power setting of 80 W (see section 4.2.1). Consequently, using 80 W seems to be more

convenient as the temperature can be controlled more easily and it would be better to utilize less amount of water to cool down the system particularly from an economic and environmental point of view. So the power setting of 80 W in addition to 50 W will be utilized in the following experiments as temperature control is easier with these two power settings.

4.5.2 Effect of low temperature on the sonochemical surface modification of Ceramic material

The chosen power setting of 80 W and 50 W has been examined at a starting temperature of 0 ºC for all the following experiments. The results obtained are compared to the results at same power setting achieved in previous experiments which have been performed at 40 ºC. Data achieved are presented as follows:

A- Weight loss

The results for weight loss at low temperature compared to the weight loss at 40 ºC are shown as follows:

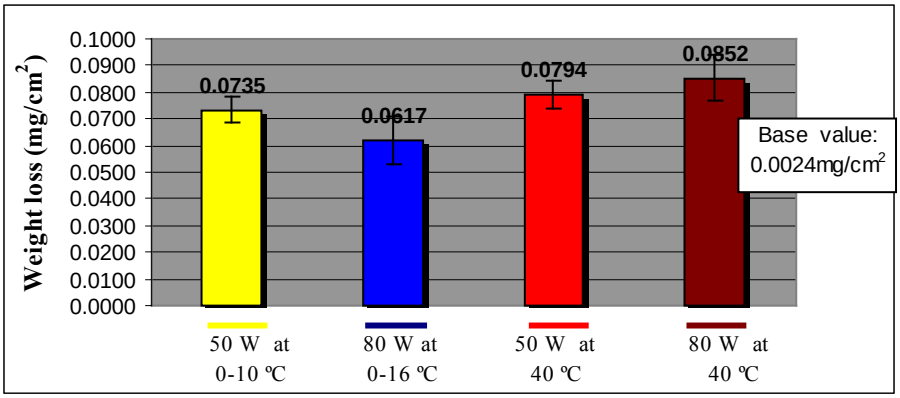


Figure (81) Effect of low temperature on weight loss for ceramic

Utilizing 80 W at 40 °C presented the higher weight loss value which was partially higher than value achieved 50 W at 40 °C. Low temperature produced less weight loss.

B- Roughness

The roughness data achieved at low temperature and compared to same power setting used at 40 ºC are presented follows:

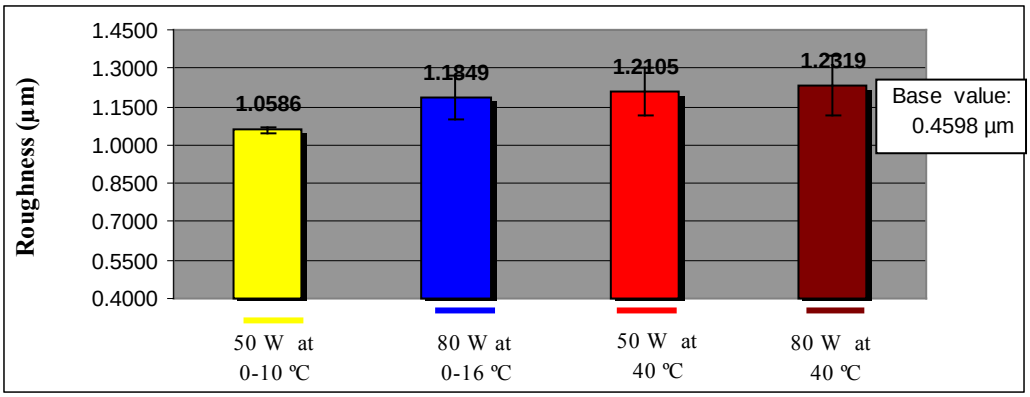


Figure (82) Effect of low temperature on roughness for ceramic material

In Figure 82, samples treated at high temperature produced higher roughness values than low temperature plaques. This was particularly observed when a power setting of 80 W was used at 40 °C.

C- <u>Adhesion (Grade)</u>

Adhesion levels for ceramic have been determined visually for low temperature experiments and compared to the values obtained at 40 ºC for same power setting . Values are shown as follows:

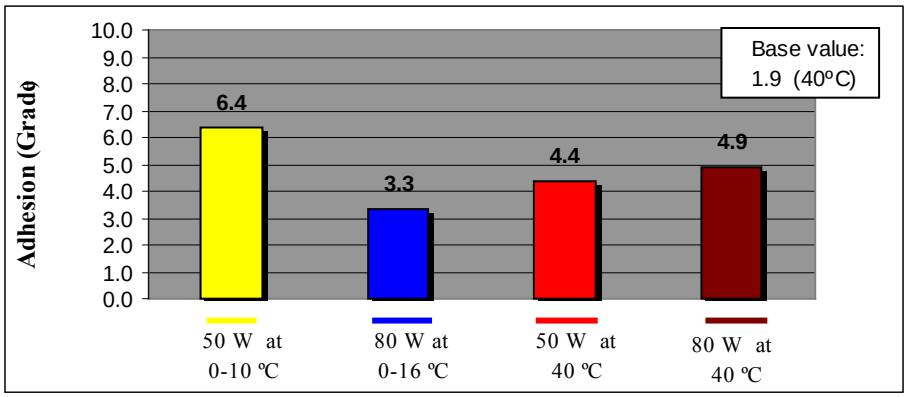


Figure (83) Adhesion grade for ceramic material at low temperature

It is obvious that higher adhesion level produced at 50 W at 0 °C compared to other conditions.

D- <u>SEM Pictures (Grade)</u>

Pictures by SEM were graded visually. Grades are compared to the values obtained at 40 ºC for same power setting and exhibited in Figure 84 as follows:

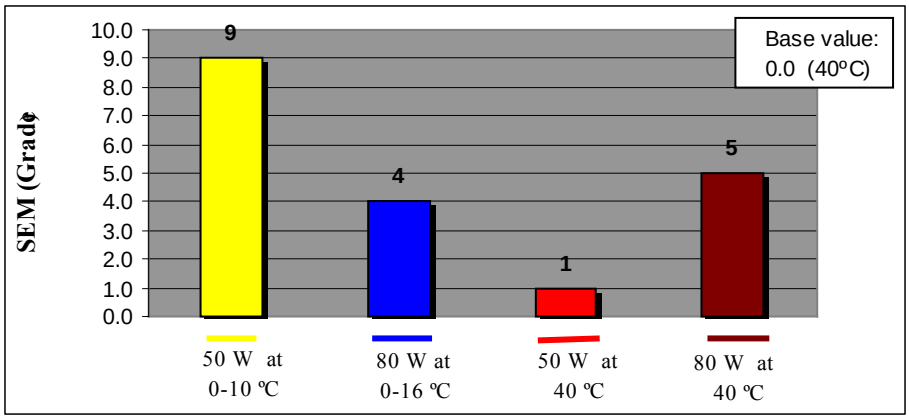
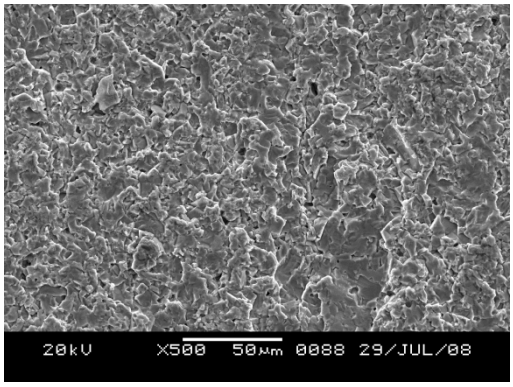


Figure (84) SEM Pictures (Grade) for ceramic material at low temperature

Figure 84 indicates that highest surface texture is observed for samples treated at low temperature with a p ower setting of 50 W compared to other values. Picture 38 shows that ceramic at low temperature produced much textured surface.



Picture (38) Ceramic surface at low temperature at 50 W

4.5.2.1 Discussion

Results achieved for low temperature experiments showed that lowering the temperature has some significant influence on the sonochemical surface modification processes compared to base line values. Weight loss (Figure 81) indicated that power setting of 50 W at 0 ºC produced higher value than with 80 W at 0 ºC. Nevertheless, weight losses these values are less than values obtained at high temperature. Although weight loss and roughness results at low temperature were lower than those results achieved at higher temperature the adhesion at 50 W at 0 °C in addition to SEM values was the highest among other conditions. It has been mentioned that

microjetting effect for cavitation increases at low temperature (Mason 1999: 12) but it did not remove higher amount of material from ceramic surface and did not produced a noticeable rough surface compared to the results obtained at 40 ºC. Instead, a high adhesion level is achieved in addition to high texture surface. This is possibly because the cavitation effect at low temperature seems to be more diffused on the surface and is distributed more evenly. Referring to Picture 38, the ceramic surface after treatment contained tiny holes on the surface, which could possibly secure a good mechanical bond with the subsequent electroless plating (Cobley, Mason and Robinson 2008).

These results are considered as significant (in term of higher values) compared to work done by Cobley and Mason (2007) at 40 °C for 60 minutes. An their work, the roughness value was approximately 0.3800 µm and SEM grade was 6 while current roughness value is 1.0586 µm and SEM grade is 9.

4.5.3 Effect of frozen samples on the sonochemical surface modification of Ceramic material

Ceramic plaques were placed in the freezer for up to 24 hours and then surface sonicated at temperatures approximating 0 ºC and 40 °C. A power setting of 50 W was utilized for all the experiments (see section 3.8). The results obtained in this section were compared to those obtained previously under the same conditions (50 W at 40 ºC and 0 °C) without freezing. Results are shown as follows:

A- Weight loss

Weight loss results obtained for ceramic frozen samples compared to not frozen samples are presented as follows:

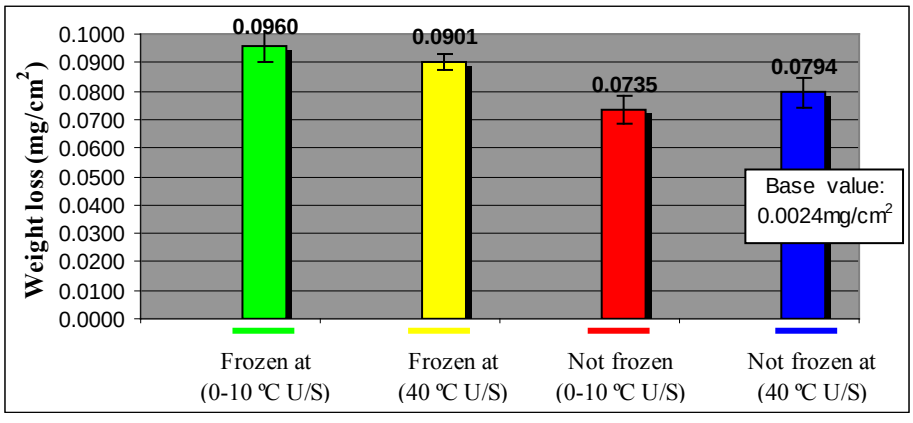


Figure (85) Effect of freezing samples on weight loss for ceramic material

Results indicate that higher weight loss value is obtained for frozen samples at low temperature which is slightly higher than the value for frozen samples at 40 ºC.

B- Roughness

Roughness results achieved for frozen samples compared to not frozen samples at same conditions are presented in Figure 86 as follows:

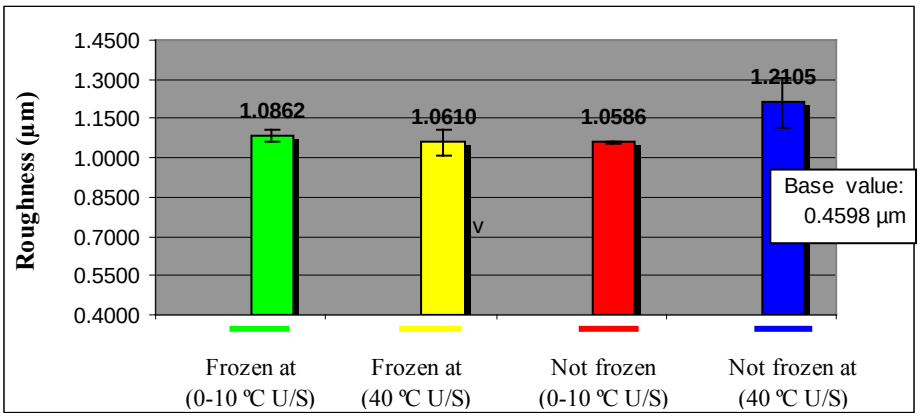


Figure (86) Effect of frozen samples on roughness for ceramic material

The surface roughness is greatest in samples that are ultrasonically treated using a 50 W power setting at 40 ^{o}C without freezing. Frozen samples also shown a high value for roughness which was a quite similar to value obtained for samples ultrasonically treated at 0 ^{o}C without freezing.

C- Adhesion (Grade)

Adhesion levels for the ceramic frozen samples have been assessed visually and compared to results achieved for not frozen samples under the same conditions. Results are presented as follows:

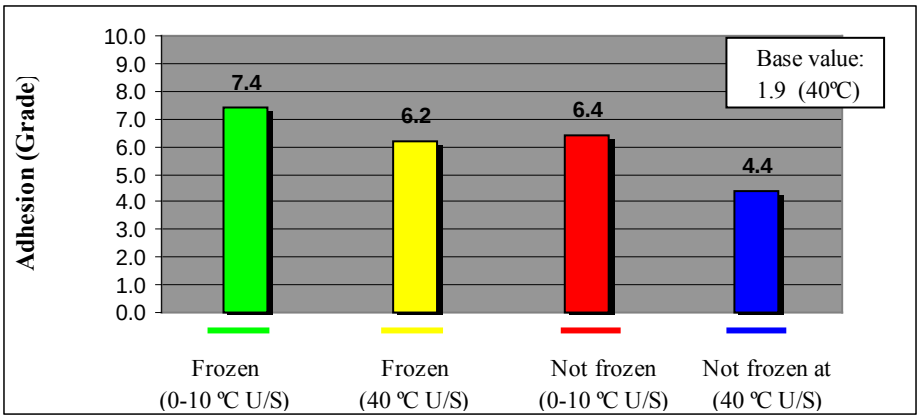


Figure (87) Effect of frozen samples on adhesion level (Grade) for ceramic material

Frozen samples ultrasonically treated at low temperature showed the highest values for adhesion level. While lowest adhesion level is obtained for not frozen samples treated at 40 ºC with a power setting of 50 W.

D- SEM Pictures (Grade)

SEM pictures have been assessed visually for frozen samples and compared to not frozen samples. Grades are exhibited as follows:

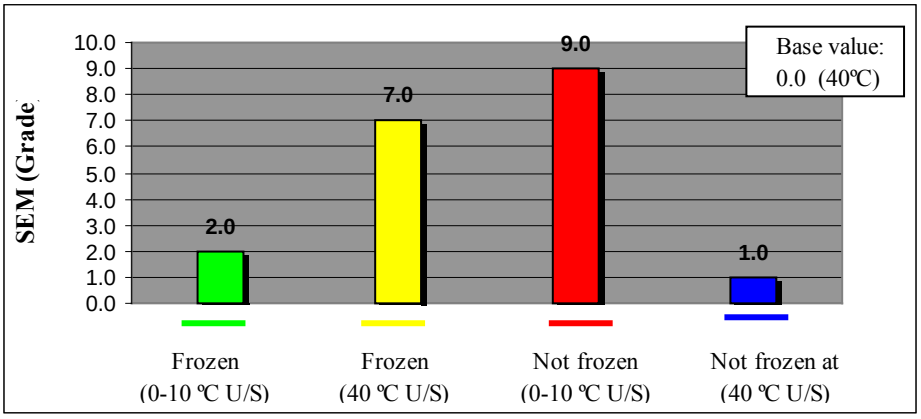


Figure (88) SEM Pictures (Grade) for ceramic material frozen samples

It is easy to see in figure 88 that highest surface morphology was produced for the not frozen samples at 0 ^{o}C. Frozen samples at 40 ºC temperature produced a value which was slightly higher than other conditions.

4.5.3.1 Discussion

Frozen samples experiments on ceramic material revealed that freezing ceramic plaques before applying ultrasound could enhance the sonochemical surface modification processes. Highest

weight loss (Figure 85) value has been achieved for frozen samples at low temperature compared to other conditions while the roughness value which was expected to be high was lower than roughness value obtained at high temperature (Figure 86). Low roughness values suggest that the surface of ceramic has been rendered to be smoother and this has been confirmed via SEM level (Figure 87) which showed the lowest value amongst all the conditions. More interesting, although the frozen samples at low temperature produced a low roughness and poorly textured surface the adhesion level achieved with this condition produced the highest adhesion level. This could be attributed to the ability of cavitation to remove more material from the ceramic surface at low temperature (Figure 85) due to microjetting threshold (Mason 1999: 12) and then it clean and remove the debris from the surface producing a smooth surface.

These results are also be considered as being remarkable in contrast with results obtained by Cobley and Mason (2007) (utilizing 60 minutes and at 40 °C) such as weight loss obtained was approximately 0.0800 mg/cm^2 and roughness was approximately 0.3800 µm while for frozen samples value is 0.0960 mg/cm^2 for weight loss and 1.0862 µm for roughness. From an economic point of view, freezing samples make the surface modification processes longer and introducing an additional expenses which are not preferable via industries.

4.5.4 Effect of adding solvents on the sonochemical surface modification of Ceramic material

Ceramic samples have been sonochemicaly surface modified with four solvent solutions. A 5 % solution for each solvent has been prepared (see 3.9) and the sonochemical processes applied with optimum power setting of 50 W that have been used at a starting temperature of 0 ºC for all the following experiments. The results obtained compared to the base line value for adding solvent (control samples) are shown as follows:

A- Weight loss

Figure 89 shows the results achieved for the effect of adding solvents on the weight loss for ceramic. Results under ultrasonic treatment compared to the base line values are presented as follows:

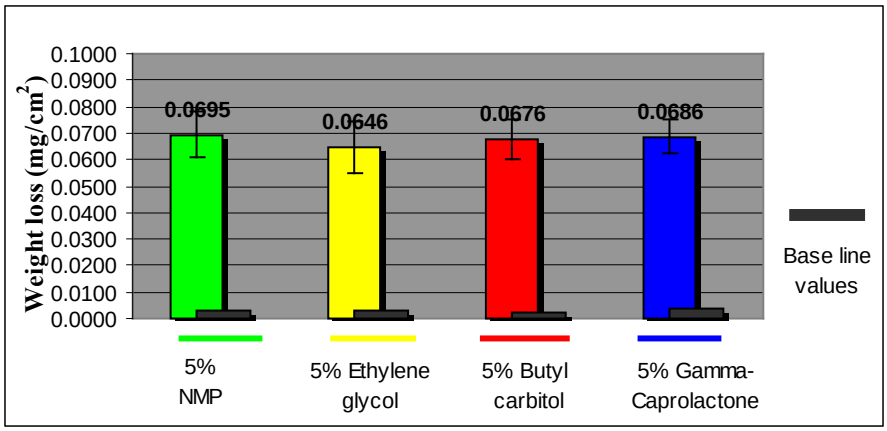


Figure (89) Effect of adding solvents on the weight loss for ceramic material

Highest weight loss for the ceramic was achieved with 5% of NMP solvent, but losses were almost similar to those obtained using other solvents. These values were higher than base line values for adding solvents.

B- Roughness

Roughness values obtained for ceramic with different solvents with ultrasound compared to base line values are shown as follows:

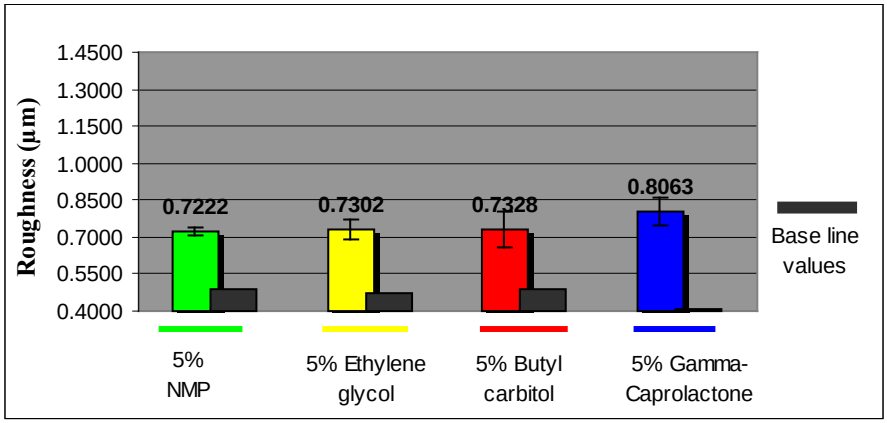


Figure (90) Effect of adding solvents on the roughness for ceramic material

The value achieved with 5 % (by volume) of gamma-caprolactone was slightly higher than values obtained with other solvents. Always, roughness data achieved following ultrasonically treatment were higher than base line values for adding solvents.

C- Adhesion (Grade)

Adhesion level has been assessed visually for samples treated under additional solvent conditions. Results compared to base line values are shown as follows:

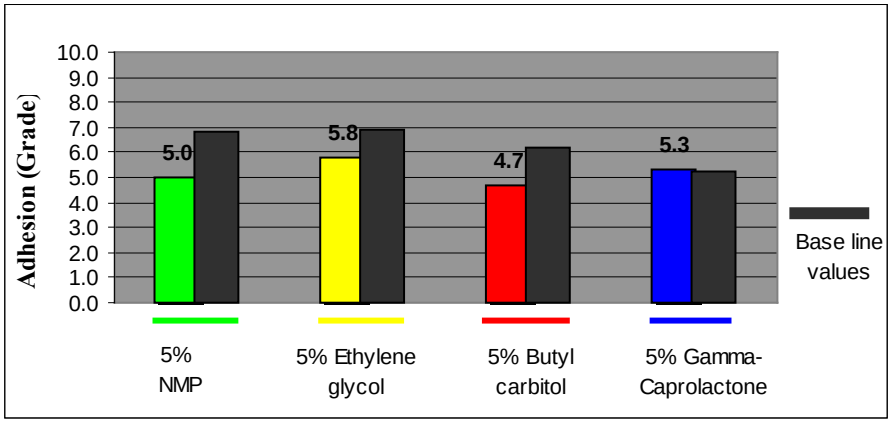


Figure (91) Effect of adding solvents on the Adhesion grade for ceramic material

Values illustrated at Figure 91 clearly indicate that examined samples presented close values for each other which were less than base level results.

D- SEM Pictures (Grade)

SEM pictures were graded visually for adding solvent samples and compared to base line value. Data presented follows:

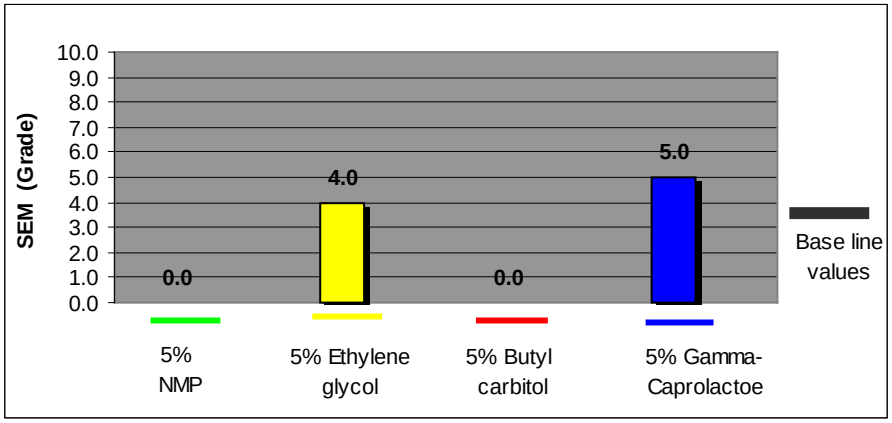
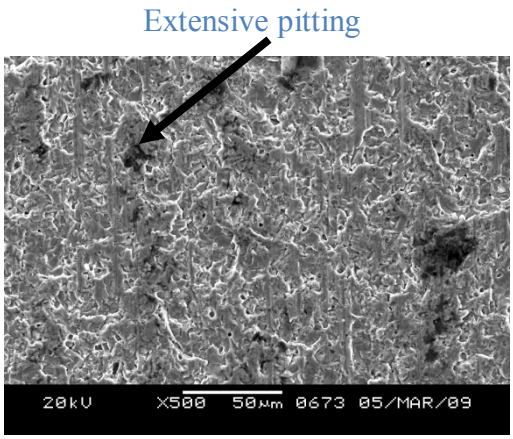


Figure (92) Effect of adding solvents on the SEM Pictures grade for ceramic material

Utilizing a 5 % gamma-caprolactone and 5 % ethylene glycol solvent has introduced a higher surface morphology while the other two solvents showed no effect on the surface morphology at all. Using gamma-caprolactone showed a slightly higher value than ethylene glycol SEM values.

In addition, Picture (39) shows the ceramic surface after ultrasonic treatment with 5 % gamma-caprolactone which produced a higher surface texture (more pitting).



Picture (39) Ceramic surface with 5 % of gamma-caprolactone at 0-2 °C

4.5.4.1 Discussion

Investigating surface modification processes of ceramic material with adding different solvents, it is observed that utilizing the solvent has an influence on the sonochemical surface modification in contrast with base line values. This influence was observed for weight loss, roughness and SEM results whereas adhesion data indicated that adding solvents associated with ultrasound produced lower adhesion level compared to base line value. The highest weight loss result was observed with 5 % NMP (Figure 89) and all the weight loss values achieved for all solvents were almost same or very close to each other. This fact was also observed for the roughness values (Figure 90) for three solvents excluding where a 5 % gamma-caprolactone is employed.

Adhesion results (Figure 91) were also somewhat close to each other remarking that 5 % ethylene glycol produced slightly higher adhesion level. SEM data indicated that the ethylene glycol and gamma-caparolactone produced a good texture surface while NMP and butyl carbitol produced same surface as base line samples. The combination of the results obtained at this part of project suggests that utilizing 5 % gamma-caparolactone seems to be the most convenient solvent which produced better values at most of analysis method. As matter of fact, although these results showed that ultrasound with adding solvents have good impact on the ceramic sonochemical surface modification in contrast with base line values but, these results were less

than those obtained for ceramic surface modification achieved at low temperature or frozen samples experiments as it can be seen from Table 8.

Analysis Method	Value with 5 % gamma-caprolactone	Value at 50 W at low temperature	Value for frozen samples with 50 W at 0 °C
Weight Loss mg/cm^2	0.0686	0.0735	0.0960
Roughness **(µm)**	0.8063	1.0586	1.0862
Adhesion (Grade)	5.3	6.4	7.4
SEM (Grade)	5	9.0	2.0

Table 8, Values for Ceramic material with 5 % gamma-caprolactone compared to the values obtained at power setting of 50 W at low temperature and values for frozen samples

4.5.5 Conclusion

Ceramic surface modification processes indicates to 100 W as the optimum power setting for surface modifying this material as at this power setting, higher results were obtained with weight loss, roughness and SEM methods which were better than at the other power settings. A power setting of 100 W only produced slightly lower adhesion level than other power settings. Nevertheless, utilizing this power setting associated with few problems that have been highlighted previously. As result, power settings of 50 and 80 W have been examined in low temperature experiments. Lowering the sonication temperature to 0 °C with a power setting of 50 W has shown a good influence particularly in term of high adhesion and SEM levels. In spite of the fact that frozen samples treated with 50 W at 0 °C introduced low roughness and SEM results, the weight loss data and adhesion level achieved for frozen samples were the most interesting results compared to all previous results obtained at previous conditions. Adding solvents experiments referred to 5 % (by volume) gamma-caparolactone as being the preferred solvent among other solvents. Nevertheless, adding solvents results were lower results in contrast with the results achieved with frozen samples treated with 50 W at 0 °C or low temperature results.

4.6 GENERAL DISCUSSION

It has been mentioned previously that the overall aim of this project was to develop an optimised sonochemical surface modification process which operates at low temperature, uses non-hazardous chemistry and short treatment times. This was achieved by investigating the optimisation of sonochemical parameters such as ultrasonic power settings, temperature, freezing the samples before treatment and the effect of adding solvents to DI water for sonochemical surface modification processes. The general discussion for each investigated parameter is as follows:

Optimum power

The optimum power setting changes with respect to the material being treated. In general, the optimum ultrasonic power setting for each individual material has been determined. For example, a power setting of 50 W was determined as optimum power setting for Noryl sonochemical surface treatment as at this power setting, higher weight loss and lowest contact angle value was observed. Moreover, roughness and gloss meter readings (Figure 56) showed very good correlation with each other with the highest roughness and low gloss meter value observed at the same power setting. Most of the results obtained at optimum power settings experiments for the different tested materials are considered as noteworthy in contrast with the results obtained by Cobley and Mason (2007).

The optimum power setting for Epoxy (high Tg) material was found to be between 50 W and 80 W at these two power settings, good results were achieved with most of the analysis methods such as weight loss, roughness, gloss meter and adhesion. For instance, the weight loss value which obtained for Epoxy (high Tg) material at 50 W at 40 °C (0.2113 mg/cm^2).

For the ABS and Ceramic material, the most optimal power setting seemed to be 100 W as slightly better results than other power settings were achieved. Due to the fact that ABS and Ceramic material surface are more harder than the Epoxy and Noryl material, there might be a need for high power setting to treat these materials as cavitation at lower power levels is insufficient and the impact of sonication is greater at higher power intensities.

Lower process temperature

Lowering the sonication temperature produced good results with all tested materials as the general sonochemical surface modification processes were enhanced. The most significant result was observed when epoxy (high Tg) material was treated with 50 W at 0 °C as most of the surface analysis results were higher than results achieved at 40 °C. For instance, the weight loss value obtained at 0 ° C was (0.3723 mg/cm^2) which matches the value obtained using the alkaline permanganate process (traditional process) (Goosey and Poole 2004) and is higher than the value of 0.3126 mg/cm^2 was obtained with 50 W at 40 °C. For Noryl material, the results achieved at low temperature were higher than results observed at 40 °C experiments such as the weight loss value (0.4713 mg/cm^2) obtained at power setting of 50 W at 0 °C is higher (double) in contrast with value obtained when 50 W is used at 40 °C (0.2113 mg/cm^2) and it is very high than weight loss results obtained via Cobley and Mason (2008) which was approximately 0.1000 mg/cm^2 using 30 minutes at 40 °C. All the other samples for ABS and Ceramic materials showed clear enhancement of the sonochemical surface treatment at lower temperature compared to the results obtained at the temperature of 40 °C. Lowering the sonication temperature was confirmed as a parameter which can enhance the cavitation effect (Mason and Peters 2002: 11).

Freezing samples before treatment

All results achieved with frozen samples for the different tested materials could be considered as being noteworthy. Freezing the Ceramic samples before the sonochemical process has been found to be a most effective method for surface modification of this material. The weight loss obtained for Ceramic frozen samples was approximately 0.0960 mg/cm^2 and the roughness was 1.0862 µm. These results were higher than those data achieved by Cobley and Mason (2007) (utilizing 60 minutes and at 40 °C) as the weight loss was 0.0800 mg/cm^2 and the roughness value was approximately 0.3800 µm. Noryl experiments introduced a more noteworthy result compared to the result obtained at 40°C or 0 °C. These results are also considered to being remarkable in contrast to those obtained by Cobley and Mason (2008) (utilizing 30 minutes and at 40 ° C), such as weight loss obtained: approximately 0.1000 mg/cm^2 and roughness was approximately 0.2500 µm while for frozen samples at 0 °C, the value is 0.6620 mg/cm^2 for weight loss and 4.3748 µm for roughness. Freezing seemed to make the surface of the material more brittle and more amenable to the sonication effects. It has been reported that freezing made

the rosemary sample more brittle and more amenable to the desired sonication effects compared to the samples stored at room temperature (Cai 2005).

However for Epoxy (high Tg) and ABS material freezing was not as effective as simply cooling to 0 °C. Freezing showed clear enhancement on the sonochemical surface treatment processes compared to the results obtained at 40 ° C, but not as high as the results obtained at low temperature (0 °C) experiments (see 4.2.3.1). From an economic point of view, freezing samples would introduce an additional step for surface modification processes which means that processes will be longer however may not be that much more beneficial.

Addition of solvents

Adding solvents showed that most of the results achieved enhanced the sonochemical surface modification processes. However the modification is enhanced by using different solvents with different substrates. For example, utilizing 5 % gamma-caparolactone was the most convenient solvent to surface modify ABS plastic as it produced better results for most of the analysis methods employed and these results were better than any results achieved with other parameters investigated previously (see 4.3.4.1). This solvent was claimed to have good influence on the swelling step for epoxy surface modify processes when applied with alkaline permanganate processes (Hirst *et al.* 2005). The weight loss value of 0.1858 mg/cm^2 which is obtained with 5 % gamma-caparolactone is considered as being significant in contrast with the value obtained by Cobley and Mason (2008) which was approximately 0.0200 mg/cm^2 and achieved at 40 °C with 30 minutes ultrasonic treatment. Employing 5 % gamma-caparolactone solvent was also most effective among for the Ceramic material but, the results with 5 % gamma-caparolactone were not as good as those results obtained for Ceramic Frozen samples experiments. For Noryl the best solvent was 5% ethylene glycol as a good results of weight loss, roughness, gloss meter contact angle and adhesion level were associated with this solvent. Ethylene glycol solvent is used widely in Asian countries in the printed circuit board industries (LaDou 2006) as a swellant agent and this solvent has low vapour pressure and this could enhance the cavitation effect (Mason & Peter 2002: 9). Finally for Epoxy samples NMP solvent was the best solvent however not as effective as the results obtained using low temperatures (see 4.2.3.1).

As a result of these experiments it can be seen that each sample has to be considered individually and as such the process needs optimisation every time with respect to temperature/ power setting/ solvent. There is no clear generalisation. Scale up may prove difficult unless all process parameters are established beforehand.

CHAPTER 5 CONCLUSIONS

5.1 CONCLUSIONS

The aim of this investigation was to observe the ability of power ultrasound to surface modify a range of dielectric polymeric materials. An ultrasound effect results from cavitational collapse of microbubbles which produces two main effects, physical and chemical effects. Physical effects include microjetting while chemical effects can be due to formation of radicals (e.g. the hydroxyl radical). These two effects are suitable for desirable surface modification processes for polymeric materials. Microjetting could produce a rough surface as the cavitation microbubbles hit the surface when it collapses and this could remove some material from the surface. In addition, this cavitation will clean the surface due to its ability to remove residue particles from the surface. Although the chemical effects associated with an ultrasonic frequency of 20 kHz are not as high as those associated with higher frequency ultrasonic equipment e.g. 850 kHz which is known to its ability to produce more radicals than 20 kHz (Mason and Peters 2002: 16), even a small oxidation occurring with this frequency at the material surface means that the chemistry of the surface could be changed. Both, physical and chemical effects can produce surface changes that secure a good adhesion with the subsequent electroless plating. The 20 kHz ultrasonic probe was used in this project for its ability to produce a higher physical effect in terms of producing more effective microjetting in addition to the chemical effects that might be occurred at the surface due to the oxidation reaction. The overall conclusions for the materials which have been surface modified are as follows:

Epoxy resin

The optimum power setting for this material is found to be between 50 W and 80 W. Applying a lower temperature (0°C) and a power setting of 50 W produced significant results in term of high weight loss, roughness and adhesion. Prior freezing of Epoxy samples showed good results compared to base line values but not as significant as those results obtained for samples ultrasonically treated at low temperature with 50 W. experiments for adding solvents revealed that a 5 % (by volume) NMP was the most efficient solvent to surface modify this material. However, all the adding solvents experiments yielded results that were not as significant as for those results obtained at low temperature using a 50 W power setting. Consequently, the most

convenient condition to surface modify Epoxy material was lowering the temperature of treatment to 0 °C and utilizing a power ultrasound setting of50 W.

ABS

It was discovered that optimization of power setting for sonochemical surface modify ABS material were very difficult to achieve. In spite of this fact, the most optimal power setting for ABS surface modification seemed to be 100 W as slightly better results than other power settings were obtained. However, more water is required and the temperature of the process increases very rapidly when using a power setting of 100 W which means that the general effects of the cavitation could be reduced(Mason and Lorimer 2002: 57). The efficiency of the probe is therefore reduced from 100 W to approximately 85 W (see section 4.2.1.1). Consequently, a power setting of 80 W and 50 W were used in the rest of the experiments. Low temperature experiments with 50 W produced a s lightly better result compared to previous experiments which also were better than the results obtained with freezing samples experiments. All solvents have good influence on the ABS surface treatment compared to base line values for adding solvent control samples. The most significant solvent is 5 % gamma-caprolactone as all results obtained with this mixture were better in achieving the desired outcome of surface modification of ABS than any results obtained in other experiments.

Noryl

A power of 50 W is the optimum power setting for surface modification of this material. Utilizing a 50 W low temperature produced more sonochemical effects than utilizing 80 W. Noryl frozen samples sonicated at 0 °C have showed more significant results compared to any previous results except for SEM results which were slightly less than the low temperature data obtained with 50 W. Utilizing 5 % (by volume) ethylene glycol solvent was the most efficient solvent amongst the other solvents because of the good results obtained for weight loss, roughness, gloss meter and contact angle. The adhesion level associated with this solvent was almost the same as the level obtained for frozen samples ultrasonically treated with 50 W.

Ceramic material

The most optimal power setting for Ceramic surface modification is 100 W. Again, more water is required and the temperature of the process increases very rapidly which means that the

general effects of the cavitation could be reduced. The efficiency of the probe is therefore reduced from 100 W to approximately 85 W. Consequently, a power setting of 80 W and 50 W were used in the rest of the experiments. Low temperature experiments with 50 W have shown that the adhesion and the SEM levels have been increased compared to other conditions. Frozen samples treated at 50 W produced very significant results in terms of weight loss and adhesion level in contrast with all other values obtained in previous experiments. Adding different solvents did not introduce any significant results compared to the results produced with low temperature or frozen samples experiments.

The main key finding for this project can be highlighted as follows:

- Ultrasound has shown the ability to surface modify all of the four tested materials. This means that this application has the potential to replace traditional treatment methods as it operates at low temperature, does not involve the use of toxic and hazardous chemicals such as chromic acid.
- Ultrasonic power setting for each material has been optimized.
- Performing the sonication processes at low temperature 0 °C can enhance the sonochemical surface modification processes particularly for epoxy (Tg resin) and noryl materials. This was an entirely novel approach.
- Freezing the samples prior to sonochemical surface treatment showed an improvement in enhanced surface modification particularly for ceramics and again this approach was novel in terms of previous work undertaken.
- Adding 5 % (b y volume) of solvents showed an enhancement of the sonochemical surface modification processes particularly with ABS material which was treated by 5 % gamma-caprolactone at low temperature 0 °C.
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5.2 FURTHER WORK

For more comparison to find the best conditions for sonochemical surface modification process, there are particular areas which would be very interesting to investigate such as:

- Further investigation into the use of ultrasonic probe which has a range of frequency such as 40 kHz since it has been proved that ultrasound can be effective for surface modify

- purpose. It has been confirmed that the generation of radicals depends on frequency which is utilized and 20 kHz produce less radicals than higher frequencies. Applying 40 kHz could generate more radicals which involve in the oxidation reaction at the surface and might form more chemical bonds between the substrate and the electroless plating.

- Increasing the concentration of the current employed solvents for up to 10% or 15% by volume. This might increase the microjetting influence or enhance the chemical effect of cavitation which however could result from increasing the vapour pressure of the solution when a g reater concentration of the solvent (low vapour pressure) is added. Consequently, this could increase the mechanical or chemical bonds between the surface and the electroless copper plating and therefore a better adhesion might be achieved and the sonochemical surface modification processes could be enhanced.

- Investigation the use of different solvents such as tripropylene glycol methyl ether (TPM) which was claimed to enhance the cavitation effect for cleaning purposes (Niemczewski 2003). The enhancement on the cavitational influence could produce more desirable surface treatment (more rough or chemistry surface) for the purpose of adhesion improvement.

- Many circuit boards currently contain holes to secure the interconnection between different layers, particularly in Multi-layer boards and these holes need to be plated with conductive material such as copper to make holes conductive. Consequently, strong adhesion between the plated material and these holes is a prime requirement. Applying the sonochemical surface modification processes to treat these holes might be a very interesting area which needs to be investigated as it could provide cheaper, non-hazardous processes in contrast with traditional methods such as using chromic acid.

- Further investigation about the chemical effect of cavitation (e.g. free radicals production) should be carry out. This can be carrying out in two ways.

- Firstly adding hydrogen peroxide which increases the formation of free radicals (hydroxyl radical) during ultrasonic treatment and this would increase the oxidation reaction on the surface of the material which means that more chemical bond will be produced at the material surface due to the oxidation reaction occurring at the surface and this might be a significant factor to improve the adhesion with the subsequent electroless plating.

- Secondly, the effect of adding some kind of free radical scavenger such as 2, 2-diphenyl-1-picrylhydrazyl (DPPH) which prevents the formation of radicals at the surface is another area which could be examined. This would investigate the effect of the absence of chemical influence (oxidation reaction) on the sonochemical surface modification processes. By another meaning, this could test the adhesion quality between the substrate and the subsequent electroless plating with the absence of the chemical bonds that occurs due to the oxidation reaction at the material surface.

In this thesis, it is clear that ultrasound does produce surface modification however what is less clear is whether that modification is based on mechanical or chemical effects. Further work is needed to identify the nature of the bonding between the metal and substrate itself. In order to identify physical bonds, techniques such as peel strength measurements method to examine the adhesion level can be considered as an indication about the physical bonds. Using Atomic Force Microscope would be more beneficial if this device could be employed as the pictures generate by this instrument gives an indication about the surface roughness and the mechanical bonds which can occurred between the surface and the plated metal. For chemical bonds, employing fourier transform infrared spectroscopy (FTIR) is a possibility as it will directly identify chemical functional groups on the surface of the material. Using of X-ray photoelectron spectroscopy (XPS) instrument is another surface chemical analysis technique that can be used to analyse the surface chemistry of the material in its "as received" state, or after some ultrasonic treatment.

At this moment in time the process is not yet ready for industrial scale up and introduction. Once the concept and approach has been proven as a viable process the next steps should include investigating the size of the process window and the process robustness (tolerance to changes to the process, such as using old chemicals or contaminated equipment to evaluate amount of control and monitoring and equipment levels required in a scaled up industrial process).

In order to scale up these processes and encourage implementation by the industry areas to focus on would include

1) Optimum or lowest temperature.
2) Most economic and green solvents.
3) Optimum settings for low power consumption and low maintenance of equipment.

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